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The self-healing composite anticorrosion coating

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Abstract

Self-healing coatings, which autonomically repair and prevent corrosion of the underlying substrate, are of particular interest for the researchers. In the article, effectiveness of epoxy resin filled microcapsules was investigated for healing of cracks generated in coatings. Microcapsules were prepared by in situ polymerization of urea–formaldehyde resin to form shell over epoxy resin droplets. Characteristics of these capsules were studied by scanning electron microscope (SEM), thermo gravimetric analyzer (TGA) and particle size analyzer. The model system of self-healing antisepsis coating consists of an epoxy resin matrix, 10 wt% microencapsulated healing agent, 2wt% catalyst solution. The self-healing function of this coating system is evaluated through corrosion testing of damaged and healed coated steel samples compared to control samples. Electrochemical testing provides further evidence of passivation of the substrate by self-healing coatings.

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Keywords: self-healing coatings; microcapsules; epoxy resin; electrochemical testin

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1. Introduction

It was well known that corrosion causes enormous industrial losses, which further deplete our natural resources. In general, organic coatings—usually organic polymers— are applied onto metallic substrates in order to avoid the detrimental effect of corrosion. During its service life, the coating undergoes changes in mechanical properties leading to formation of microcracks which subsequently propagates and exposes substrate to atmospheric moisture and oxygen[1]. Paint coatings can be considered as multi-layered systems of composite materials, comprising binders and pigments. Hence, the concept of self-healing of cracks, as reported for composites, can be adopted for coatings to provide longer service durability. Different techniques have been developed and adopted for repairing detectable damages on the coatings. However, these conventional repairing methods are costly, time consuming, and require reliable detection techniques and a skilled workforce. In addition, they are mainly applicable to the repair of external and accessible damages instead of the internal and invisible microcracks[2]. Development of self-healing polymeric materials is thus expected to fill this technological gap[3-6].

Research on self-healing polymers has demonstrated repairing of bulk mechanical damage of a product as well as dramatic increase of its service life[7-10]. The most common approaches for self-healing of the polymer coating layer involves incorporation of self-healing reagents within a vast amount of small brittle vessels[11-16], and then, the vessels with the self-healing reagents are mixed into the polymeric matrix. These vessels fracture upon loading of the coating, releasing the low viscosity self-healing reagents to the damaged area for curing and filling of the microcracks[17]. Recently, there has been growing interest in use of microencapsulated reactive monomers for healing of cracks generated during service of functional coatings.

Here, we report our results on development of self-healing coatings with microencapsulated epoxy resins. The polyoxymethylene urea (PMU) microcapsules containing the mixture of epoxy resins BGE and E-51 are produced by in–situ polymerization technology. In the polymerization, the hot water dilution is used to distract the microcapsules, which avoided the polymer dispersant effect on the microcapsules performance.

2. Materials and methods

2.1. Preparation and characterization of microcapsules

At room temperature, 5 g urea, 0.5 g ammonium chloride and 0.5 g resorcinol were dissolved in a round flask with 200 ml deionised water. The pH was adjusted to approximately 3.5 by using 3.6 wt% solution of hydrochloric acid in deionised water. Then 20 ml core material (epoxy BGE and E-51) was added slowly to form an emulsion and allowed to stabilize for 10min under agitation. After stabilization, 12.67 g of 37 wt% aqueous solution of formaldehyde was added. The flask was suspended in a temperature-controlled water bath with an external temperature probe. The emulsion was covered and slowly heated and maintained at 60□under stirring at 900rpm for 4 h. Contents were cooled to ambient temperature; the suspension of microcapsules was rinsed with deionized water and vacuum filtered. Microcapsules were dried under vacuum before further analysis

Surface morphology, size and shell thickness of microcapsules were analyzed by scanning electron microscopy, (SEM, QUANTA 200).The dried powders of sieved microcapsules were placed on a conductive carbon tape attached to a mounting piece for imaging. The size distribution of microcapsule was carried out with a particle size analyzer (Beckman Coulter LS 13320). The samples were also analyzed using thermo gravimetric analyzer (TGA, NETZSCH STA 449C) in nitrogen environment with a sample weight of about 15mg. Heating rate was maintained at 10□/min in the temperature range of 30–500□. The flux of nitrogen of methods is 60 ml/min.

2.2. The self-healing experiments of anticorrosion coating with microcapsules

The model system consists of an epoxy resin matrix, 10 wt% Urea-formaldehyde (UF)-microencapsulated healing agent, 2 wt% phase-separated catalyst solution. The percentages of each component are selected based on our prior experiments on self-healing of bulk materials.

All coatings were applied to cold-rolled steel sheets, using a micrometer-controlled doctor blade. Coating solutions were applied to one end of the substrate, and the doctor blade was used to spread a uniform-thickness coating.

The self-healing function of this coating system is evaluated through corrosion testing of damaged and healed coated steel samples compared to control samples. Damage is induced by hand scribing through the 200μm thick coating and into the substrate using a bistoury blade (Fig. 1.and Fig. 2.). Following the scribing procedure, samples were allowed to heal at 60□for 72 h, and then immersed in 5 wt% aqueous NaCl solution.

Electrochemical testing provides further evidence of passivation of the substrate by self-healing coatings. In these experiments, samples were disposables like Fig.3; the coated steel sample serves as one electrode in an electrochemical cell (Fig. 4). The steady-state conduction between the coated metal substrate and a platinum electrode held at 2V through an aqueous electrolyte (3.5 wt %NaCl) was measured (Fig. 4).

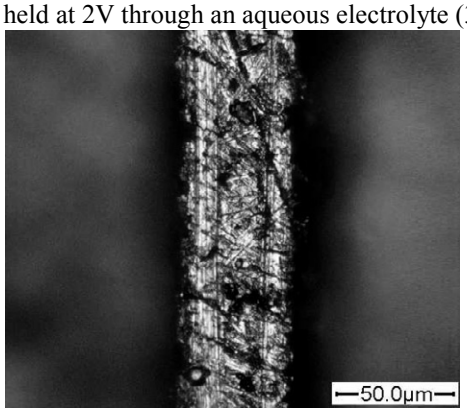

Fig.1.OM images of sample being scribed

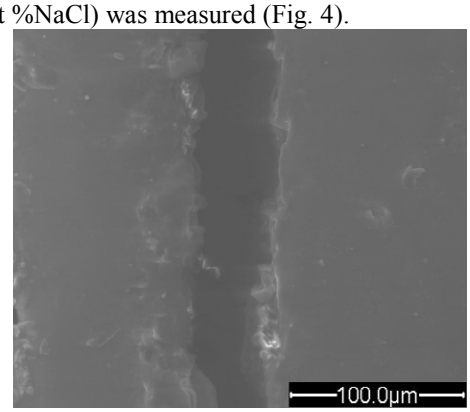

Fig.2. SEM images of the scribed region of the coating

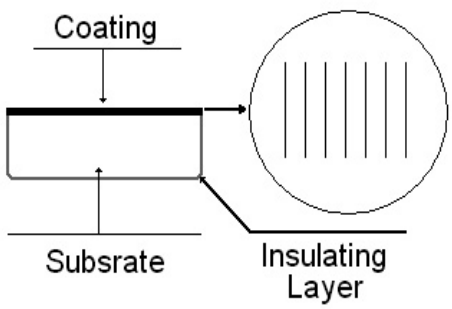

Fig.3. Schematic diagram of samples being scribed

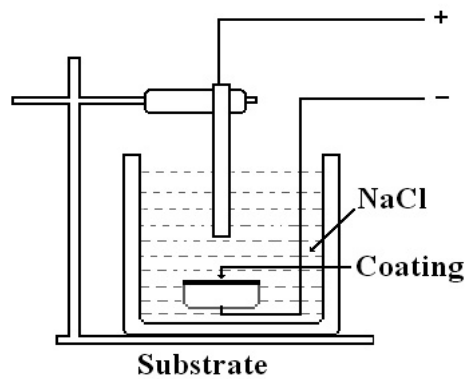

Fig.4. Schematic diagram of the electrochemical test

3. Results and discussion

3.1. Analysis of microcapsules characterization

Surface morphology and size of microcapsules were analyzed by scanning electron microscopy. Fig. 5 shows the SEM micrographs of (a) capsule size and (b) microcapsule shell morphology. The size of microcapsule is about 100 μm; the shell morphology of the capsule is granulated. Fig. 6 shows the particle size distribution of microcapsules. The size ranges from 25 to 250μm. However, most of the particles fall in the size range around 120μm. This is quite satisfactory for using in paints. Upon thermo gravimetric analysis (TGA) exhibit a primary weight loss starting near the boiling point of chlorobenzene (70℃), and a secondary weight loss starting at 225℃. The microcapsules are chemically stable below 225℃, indicating that the prepared microcapsules have a good thermal stability.

3.2. Analysis of corrosion testing

Form optical microscopy and scanning electron microscopy (SEM) images of the scribe region in control and self-healing coatings reveals the morphology of the repaired coating, all control samples rapidly corroded within 72

h, and exhibited extensive rust formation, most prevalently within the groove of the scribed regions, but also extending across the substrate surface (Fig. 8 and Fig.9). In dramatic contrast, the self-healing samples showed no visual evidence of corrosion, even 72 h after exposure. Flow of healing agent and catalyst into the scribe and recoating of the substrate is readily apparent (Fig. 10 and Fig.11). Separate control tests reveal that the presence of both the healing agent and catalyst are necessary for self-healing functionality. Removal of either phase results in a coating which corrodes rapidly, providing a clear indication that simple reflow of one of the phases into the crack is not sufficient to prevent corrosion.

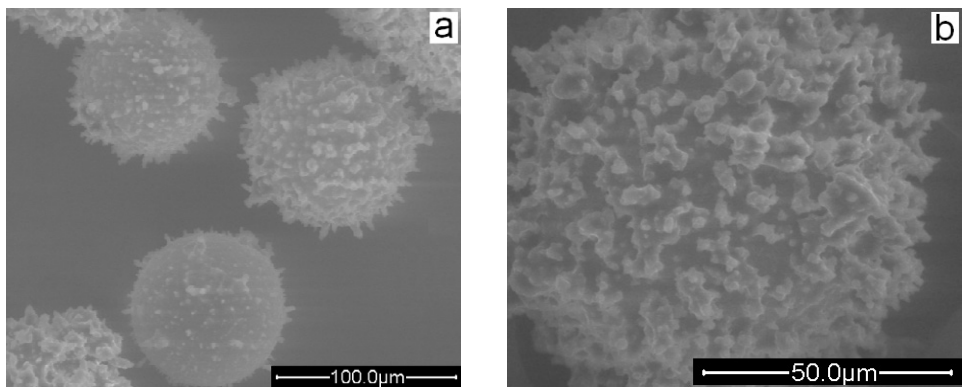

Fig.5. SEM micrographs: (a) size of the microcapsules (b) the rough exterior shell wall

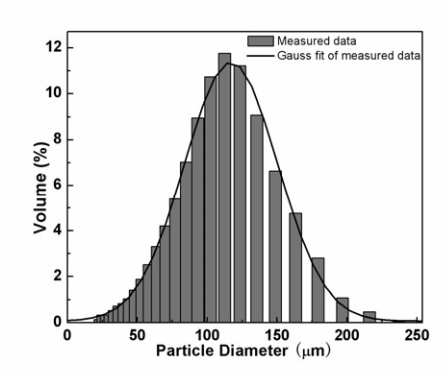

Fig.6.Size histogram for microcapsules

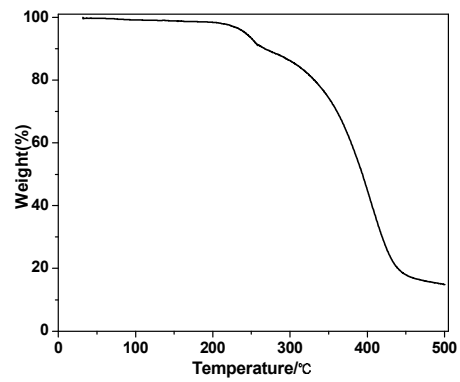

Fig.7.TGA analysis of microcapsules

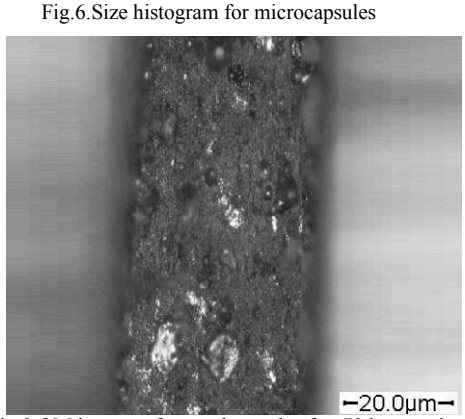

Fig.8.OM images of control sample after 72 h corrosion

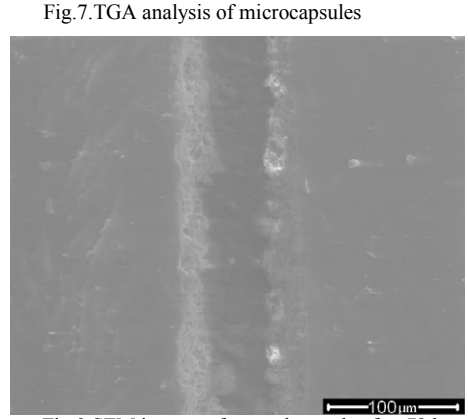

Fig.9 SEM images of control sample after 72 h corrosion

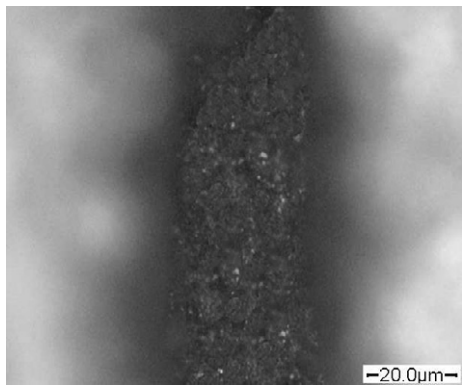

Fig.10.OM images of self-healing coating after 72 h corrosion

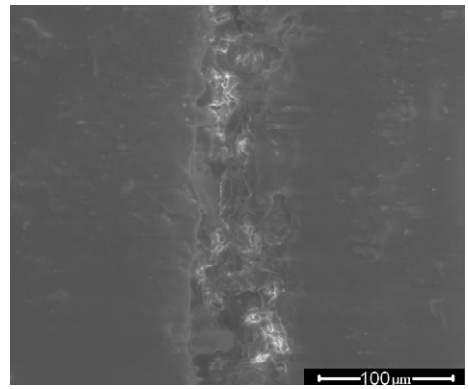

Fig.11. SEM images of self-healing coating after 72 h corrosion

3.3. Analysis of electrochemical testing

In the electrochemical testing of the scribe region in control and self-healing coatings, the current passing through the control and self-healing coatings before scribing were nearly identical (2.25033×10^{-6}A). After scribing, samples were allowed to heal and were tested in the electrochemical cell. From figure 12, the current passing through the scribed control samples was quite large (5.731×10^{-4}A), compared to the undamaged state, and we noted rapid gas evolution from the scribed region during the test. The self-healing samples showed a dramatically reduced current (2.25033×10^{-6}~4.36013×10^{-6}A).Self-healing coating show the most same current as samples had no scribing, and no gas evolution is observed from the self-healing sample.

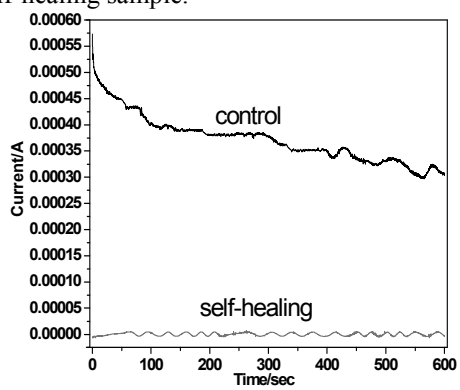

Fig.12.Current versus time for scribed control and self-healed sample.

4. Conclusions

Core material (epoxy BGE and E-51) had been successful encapsulated into urea–formaldehyde shell. Microcapsules having sufficient strength to withstand shear generated during mixing in to paint and paint application. The rough morphology of microcapsule shell has provided good anchoring between microcapsule and paint matrix. Microcapsules in paint films released healing material, which during cracking healed cracks efficiently with satisfactory anticorrosive properties. In a word, the cracks in an anticorrosion coating were successfully healed when epoxy resin was released from microcapsules ruptured under simulated mechanical action. Epoxy resin healed area was found to prevent corrosion of the substrate.

Acknowledgements

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