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Self-healing coatings containing microcapsule

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ABSTRACT

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 3D measuring laser microscope, particle size analyzer, Fourier-transform infrared spectroscopy (FTIR) and differential scanning calorimeter (DSC) to investigate their surface morphology, size distribution, chemical structure and thermal stability, respectively. The results indicate that microcapsules containing epoxy resins can be synthesized successfully. The size is around 100 μm. The rough outer surface of microcapsule is composed of agglomerated urea–formaldehyde nanoparticles. The size and surface morphology of microcapsule can be controlled by selecting different processing parameters. The microcapsules basically exhibit good storage stability at room temperature, and they are chemically stable before the heating temperature is up to approximately 200 °C. The model system of self-healing coating consists of epoxy resin matrix, 10 wt% microencapsulated healing agent, 2 wt% catalyst solution. The self-healing function of this coating system is evaluated through self-healing testing of damaged and healed coated steel samples.

1. Introduction

Corrosion degradation of materials and structures is one of the important issues that lead to enormous industrial losses. The use of paint coatings is the most common method for corrosion prevention [1–3]. The main role of the coating is to protect metal forming effective barrier against corrosive species present in different environments [4]. Paints and coatings degrade fast due to mechanical damage. Development and coalescence of microcracks in the coating would cause catastrophic failure. These areas are highly susceptible to corrosion. After corrosion started the polymer coating itself cannot protect the defective zone and is not able to stop propagation of the defect.

There are many repair techniques that have been developed and adopted for repairing visible or detectable damages on the coatings. However, these conventional repair methods are generally time consuming, complicated, and require reliable detection techniques. They are mainly applicable to the repair of external and accessible damages instead of the internal and invisible microcracks [5]. The development of self-healing polymeric materials is expected to fill this technological gap [6–9].

Research on self-healing polymers has demonstrated repairing of bulk mechanical damage of a product as well as dramatic increase of its service life [10–12]. The most common approaches for self-healing of the polymer coating layer involves incorporation of self-healing reagents within a vast amount of microcapsules [13–17], and then, they are mixed into the polymeric matrix. These microcapsules fracture upon loading of the coating, releasing the low viscosity self-healing reagents to the damaged area for curing and filling of the microcracks [18]. Therefore, self-healing of defects in coatings is necessary to provide long-term protection effect and to prolong the maintenance intervals.

Here, we report our work on development of self-healing coatings with microencapsulated epoxy resin, and demonstrate its effectiveness for both model and industrially important coating systems.

2. Experimental

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 501 and E-51) was added slowly to form an emulsion and allowed to stabilize for 10 min 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 °C under stirring at 700 rpm for 4 h. Contents were cooled to ambient temperature; the suspension of microcapsules was rinsed with deionized water and

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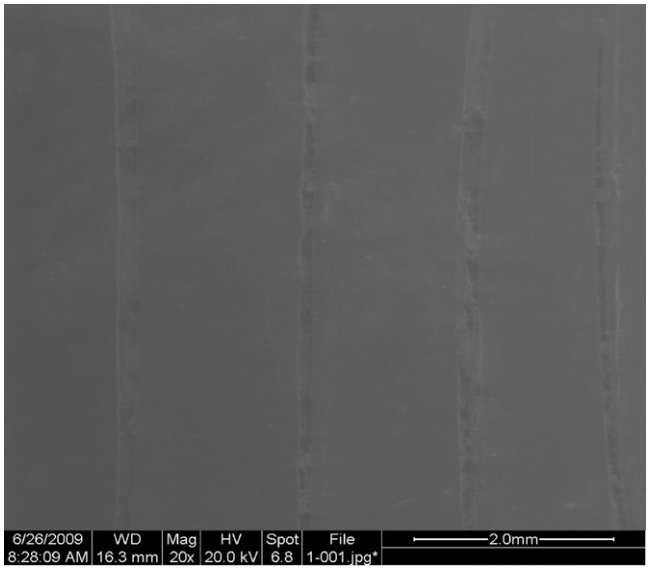

Fig. 1. SEM images of the scribed region of the coating.

vacuum filtered. Microcapsules were dried under vacuum before further analysis.

Surface morphology and size of microcapsules were analyzed by 3D measuring laser microscope (LEXT OLS4000). The dried powders of sieved microcapsules were placed on a glass slide 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 differential scanning calorimeter (DSC, CDR-4P) in nitrogen environment with a sample weight of about 15 mg. Heating rate was maintained at 10 °C/min in the temperature range of 30–500 °C. The flux of nitrogen of methods is 60 ml/min. Fourier-transform infrared (FTIR) spectra were obtained using a FTIR spectrometer (Bruker, EQUINOX 55) to identify the chemical structure of the specimen, which was prepared by grinding the sample with a potassium bromide (KBr) or by attaching sample to a KBr disc.

The model system consists of an epoxy resin matrix, 10 wt% urea–formaldehyde–microencapsulated healing agent, 2 wt% latent curing agent 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. The self-healing function of this coating system is evaluated through healing testing of damaged and healed coated steel samples. Damage is induced by hand scribing through the 200 μm thick coating and into the substrate using a bistoury blade (Fig. 1). Following the scribing procedure, samples were allowed to heal at 60 °C for 72 h.

3. Results and discussion

The microcapsules size analysis was performed by 3D measuring laser microscope and particle size analyzer. The surface morphology of microcapsules was investigated by 3D measuring laser microscope, as shown in Fig. 2. The images revealed that the capsules were spherical in shape. The surface of microcapsule is rough and scraggly, and it is an agglomeration of UF nanoparticles. Fig. 3 shows the size distribution of microcapsules. The microcapsule size is in a wide range of 20–200 μm. The reason for this is that the fluid flow around the propeller is turbulent, in the region of flow away from the propeller, many larger microeddies exist, and

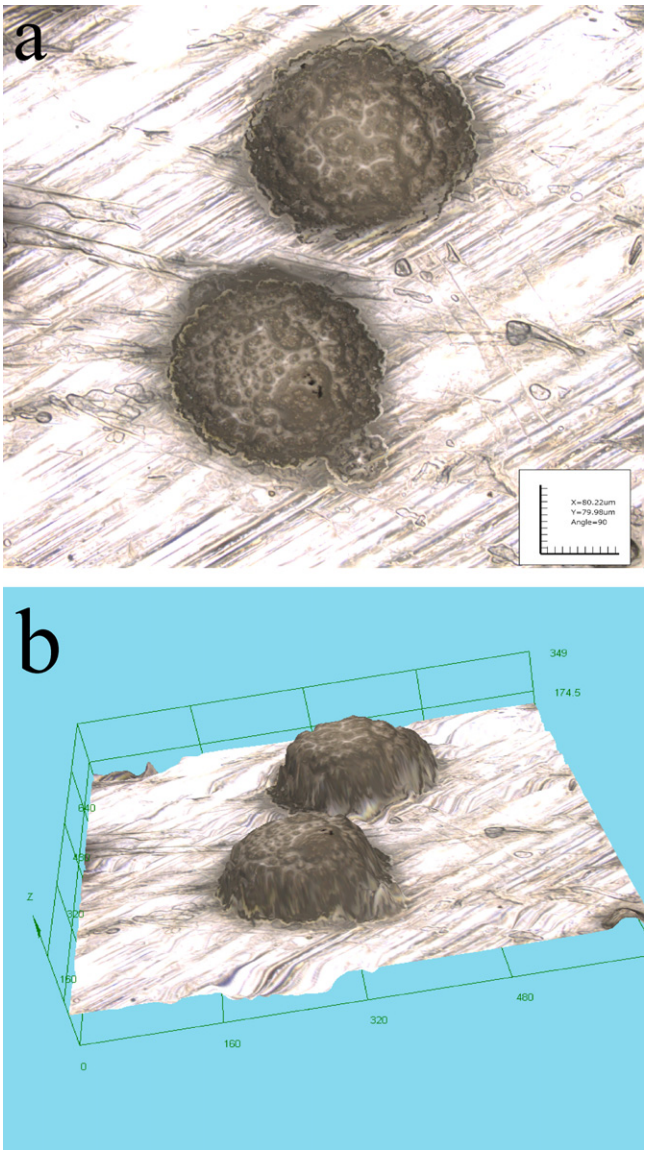

Fig. 2. Surface morphology of microcapsules: (a) two-dimensional graph; (b) three-dimensional graph.

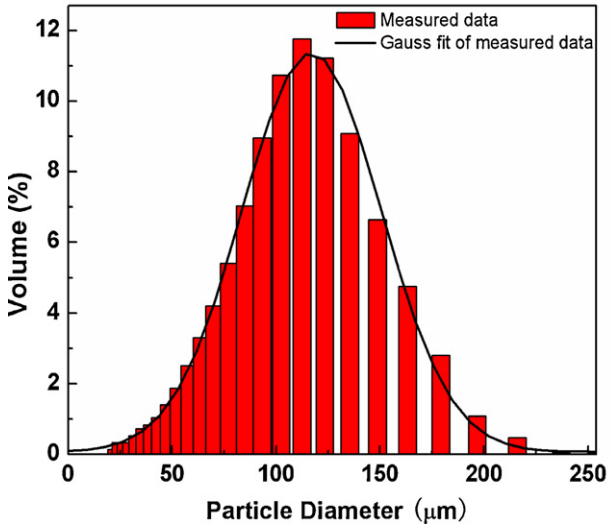

Fig. 3. Size histogram for microcapsules.

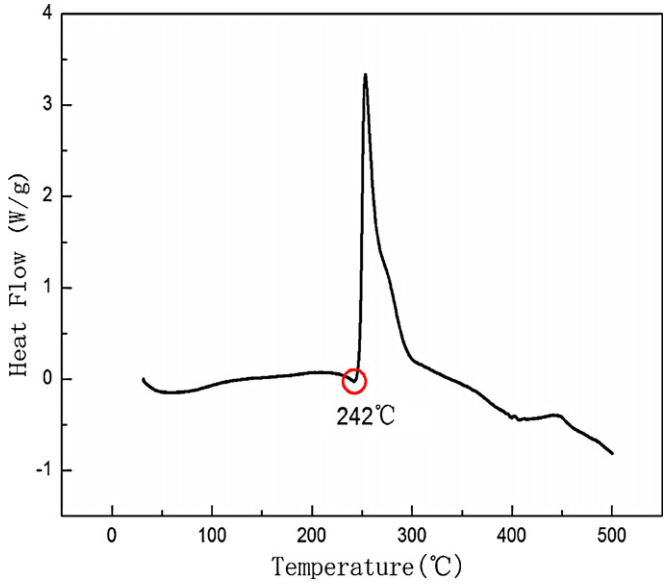

Fig. 4. DCS analysis of microcapsules.

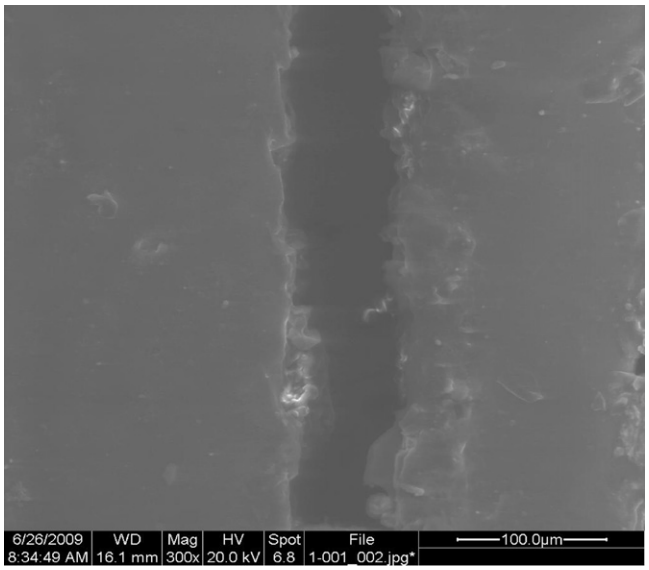

Fig. 6. SEM images of sample before healing.

in the vicinity of the propeller blades, many smaller microeddies exist, which result in a wider length scale [15]. In this study, most of the particles fall in the size range around 100 μm. This is quite satisfactory for its use in self-healing coating.

The thermal property of microcapsules plays an important role in their applications in functional coatings. Fig. 4 shows the DSC curve of microcapsule. Evidently, the thermal stability of microcapsules containing the mixture of epoxy resins was excellent. The peak at temperatures between 242 °C and 300 °C is mainly due to the decomposition of the wall shell. Obviously, the prepared microcapsules have a good thermal property.

The FTIR spectra of the core material, microcapsules, and shell material that was synthesized under the same conditions as those employed for making the microcapsules, were collected in Fig. 5. Clearly, strong absorptions appear at 3384 cm^{-1} of the spectrum of the microcapsules, which represent the stretching modes of N–H and O–H of urea–formaldehyde resin. Those of epoxy including the bands of terminal epoxide group at 913 cm^{-1} and 831 cm^{-1}, benzene ring stretching vibration appeared at 1248 cm^{-1} and 1510 cm^{-1} are also perceivable in the spectrum of the microcapsules. In view of above facts, it is established that the mixture of epoxy resin as the core materials has been successfully encapsulated in urea–formaldehyde shell.

The microcapsules were incorporated in the paint film, these capsules rupture and release healing agent during crack formation and reacts with catalyst present in the coating leading to crack repair to restore anticorrosion properties. It is observed that the shell surface of microcapsules is very

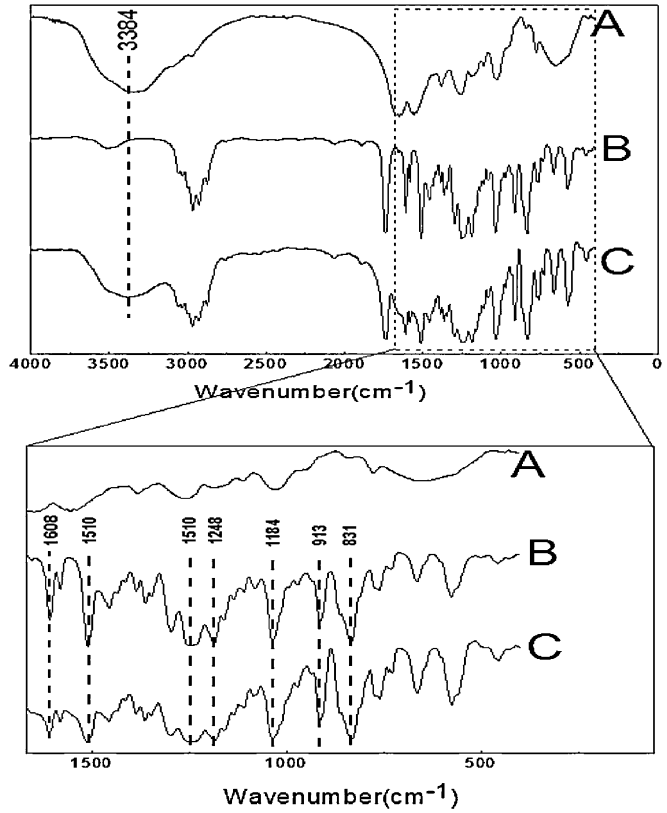

Fig. 5. FTIR spectra: (a) shell material; (b) core material; (c) microcapsules.

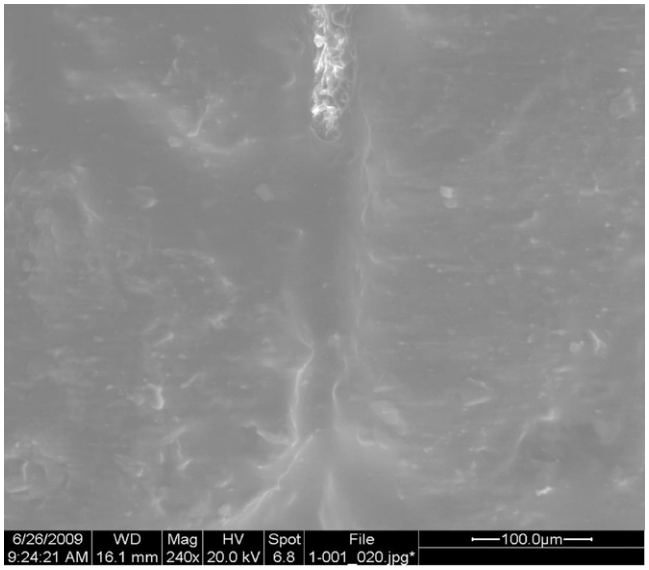

Fig. 7. SEM images of sample after healing.

rough (Fig. 2a), which will provide good bonding with the film matrix. This facilitates in breaking of microcapsules under stress due to cracking. Scanning electron microscopy (SEM) images of the scribed region in self-healing coatings samples revealed the morphology change of the repaired coating. It is observed that the initial open length of the crack is maximum (Fig. 6), which gradually reduced and completely filled after 72 h (Fig. 7).

4. Conclusions

This research has shown potential for developing self-healing coating by incorporating microcapsules into paints. Microcapsules having sufficient strength to withstand shear generated during mixing into paint and paint application. The rough morphology of microcapsule shell has provided good anchoring between microcapsule and paint matrix. The microcapsules basically exhibit good storage stability at room temperature, and they are chemically stable before the heating temperature is up to approximately 200 °C. It has been shown that the epoxy resin is released when the microcapsules are ruptured under simulated mechanical action.

Acknowledgements

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