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Preparation and characterization of microcapsule containing epoxy resin and its self-healing performance of anticorrosion covering material

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Microencapsulated healing agents that possess adequate strength, long shelf-life, and excellent bonding to the host material are required for self-healing materials. The *in situ* encapsulation method is demonstrated over an order of magnitude size reduction for the preparation of urea-formaldehyde (UF) capsules filled with a healing agent, a mixture epoxy resin of the epoxy 711 and E-51. Capsules with diameters as small as about 100 μm are achieved under the agitation rate of 800 r min^{-1}. The capsules possess a uniform UF shell wall (4 μm average thickness). By using the analysis of scanning electronic microscope (SEM), thermal analysis (TG-DTA) and FTIR, the characteristics of the microcapsules were investigated respectively. Successful self-healing has been demonstrated for anticorrosion covering materials with microcapsules.

microcapsule, epoxy resin, urea-formaldehyde, self-healing materials

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Microcapsules and microcapsule technology have been widely employed in a series of fields. They have been utilized for sustained drug release [1,2], preservation of flavours [3,4], electro phoretic display applications [5], intumescent fire retarding powders [6,7], biotechnology [8,9] and inorganic metal salt catalyst [10], etc. And there has been growing interest in use of microencapsulated materials for the healing of cracks generated during the service of polymer based composite materials [11,12]. The working principle is based on the fact that microcapsules containing healing agents were incorporated in the target polymer. These capsules rupture and release healing agents during crack formation and react with catalyst present in the composites leading to crack repair to restore mechanical properties. The poly (urea-formaldehyde) (PUF) microcapsules are synthesized for self-healing of materials. Now several groups synthesized the microcapsules with the dicyclopentadiene (DCPD) [13] and epoxy [14–16]. Although the catalyst of healing agents is more valuable, it is not suitable for the mass production and large-scale application. In this experiment, two kinds of epoxy resins (E-51 and 711), were used as the core materials of the microcapsule.

Now the main anticorrosion way is to use the paints to keep the surface of substrates for corrosion protection. However, during its service life, the anticorrosion coating undergoes changes in mechanical properties leading to the formation of microcracks which subsequently propagates and exposes substrate to atmospheric moisture and oxygen. This action results in accelerated disbonding of the paint and flake formation from the metal coating interface. Anticorrosion coatings can be considered as a special class of composite materials, so the concept of self-healing of cracks, as reported for composites, can be adopted for coatings to provide longer durability.

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Here, we report our works on the development of self-healing coatings with microencapsulated healing agents. In this study, microcapsules with urea-formaldehyde as a shell and a mixture epoxy resin of the epoxy 711 and E-51 as the core were synthesized by *in situ* polymerization. The structure and performance of the microcapsules were analyzed. Efficacy of these microcapsules in healing of cracks in anticorrosion covering materials has been demonstrated.

1 Materials and methods

(i) Preparation of microcapsules. Microcapsules containing epoxy 711 and E-51 were prepared by *in situ* polymerization. At room temperature, 200 mL of deionised water was slowly added into 1000 ml beaker. Under agitation 5 g urea, 0.5 g ammonium chloride and 0.5 g resorcinol were dissolved in solution. The pH was adjusted to approximately 3.5 by using the solution of hydrochloric acid in deionised water. Then 20 mL of mixture epoxy resin of the epoxy 711 and E-51 ($M_{711}/M_{E\text{-}51}$=1/5) 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 emulsion was heated and maintained at 60°C under stirring at 800 r min^{-1} for 4 h. Contents were cooled to ambient temperature. Microcapsules from the suspension were recovered by filtration under vacuum. These were rinsed with water. The capsules were dried under vacuum.

(ii) Analysis of microcapsule size and shell morphology. Microcapsule size analysis was carried out with a particle size analyzer (Beckman Coulter LS 13320). Surface morphology, shell thickness and the size of microcapsules were determined by scanning electron microscopy (SEM, QUANTA200). Microcapsule was mounted on adhesive tape and ruptured with a razor blade for shell thickness measurement.

(iii) Analysis of microcapsule chemical construction. The chemical construction of microcapsule was analyzed by the Fourier Transform Infrared spectrophotometer (Bruker, EQUINOX 55). The solid shell material collected after extraction was mixed with KBr, and then they were squeezed to the flake. After dried, the microcapsules mixed with KBr were grinded to the flake, which was analyzed by the infrared spectrophotometer. In the same way, the chemical construction of core materials (epoxy resin 711 and E-51) was analyzed.

(iv) Thermal analysis of microcapsules. Microcapsules were analyzed using thermal analysis (TG-DTA, NETZSCH STA 449C) in nitrogen environment with a sample weight of about 7.5 mg. Heating rate was maintained at 10 K/min in the temperature range of 30–500°C. The flux of nitrogen of the method is 60 mL/min.

(v) Salt spray experiment of anti corrosion paint with microcapsules. Corrode liquor preparation: 50 g sodium chloride was dissolved in deionised water. Then 0.26 g $CuCl_2 \cdot H_2O$ was added to the solution. The pH was adjusted to approximately 3.1–3.5 by using glacial acetic acid.

Salt spray cabinet: temperature, (50±2)°C; spray measure, 1–2 mL/h·80 cm^2; relative humidity, 95%–100%; continuing spray 120 h.

Clean steel panels, with size of 3 mm×3 mm×35 mm, were coated on one side by brush to obtain epoxy aluminum priming coating. The microcapsules and firming agent were incorporated in epoxy anticorrosion paint solution. After solidified, cross-cut was made on panels and kept at ambient of salt spray. A composition without microcapsules was prepared as a control. Specimens coated with both compositions were exposed for a period 120 h in salt spray cabinet for evaluation of corrosion protection.

2 Results and discussion

2.1 Analysis of microcapsules size and shell morphology preparation of microcapsules

The microcapsule size analysis was performed by using two different methods, SEM and a particle size analyzer (Beckman Coulter LS 13320). Figure 1 and Figure 2 show the SEM micrographs: (a) capsule shell thickness (b) size and shell morphology. The SEM images revealed that the capsules were spherical in shape, with non-porous shell wall. The surface of microcapsule is rough and scraggly, and it is composed of PUF nanoparticles protruding from the surface. In the micrographs, the size and shell thickness of microcapsules were also observed. The size was around 100 μm; the shell thickness is around 4 μm. Figure 3 shows the particle size distribution of microcapsules. The microcapsule size is in a wide range of 20–200 μm. The reason is that the fluid flow around the propeller is turbulent; in the region of flow away from the propeller; many larger microeddies exist, and in the vicinity of the propeller blades, many smaller microeddies exist, which result in a wider length scale [17,18]. The microcapsule size can be controlled by adjusting agitation rate. In this study, most of the particles fall in the size range around 100 μm. This is quite satisfactory for the use in self-healing of material.

2.2 Analysis of infrared spectroscopy

It is seen from the FTIR spectra of shell material and urea-formaldehyde resin (Figure 4) that both are closely matching at the characteristic peaks of an N-H stretching vibration at 1554 cm^{-1}, a C=O stretching vibration at 1648 cm^{-1}, and a C-H stretching vibration at 1460 cm^{-1}. C-N stretching vibrations are shown at 1286 and 1142 cm^{-1}. The O-H peak is shown as a broad absorption peak at 3400–3200 cm^{-1}. This spectrum confirms that shell material is made of urea-formaldehyde polymer. The FTIR spectrum of urea-formaldehyde resin is also matching with spectrum reported in the literature. Spectra of microcapsule and the

core materials have also been found matching (Figure 5) at characteristic peaks for C=O, saturated C–H, double methyl radical $-C(CH_3)_2$ and frame of benzene ring stretching vibrations. Besides the spectra of microcapsule have the same characteristic peaks of urea-formaldehyde resin (Figure 4(b), Figure 5(b)). In view of the above it is established that the core materials have been successfully encapsulated in urea-formaldehyde shell.

2.3 Thermal stability of microcapsules

The thermal stability of microcapsules plays an important role in their applications in self-healing composites materials. Figure 6 shows the TGA and DSC curve of microcapsule. In the DSC curve of microcapsules, there are two endothermic peaks and two exothermic peaks appeared. For the two endothermic peaks, the first endothermic one below 100°C is due to the evaporation of water and free formaldehyde. The second one at temperatures between 225 and 248°C is due to the decomposition of shell materials [19]. With respect to the two exothermic peaks, the first one at temperatures between 250 and 300°C is due to the polymerization reaction of core material. The second one is at 450°C, which perhaps due to the continuous polymerization reaction of core material. The TGA curve of microcapsules

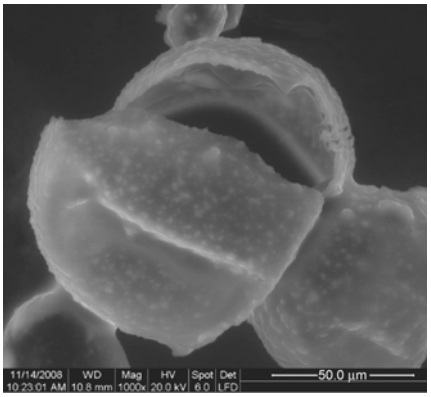

Figure 1 SEM micrographs: Shell thickness of microcapsules.

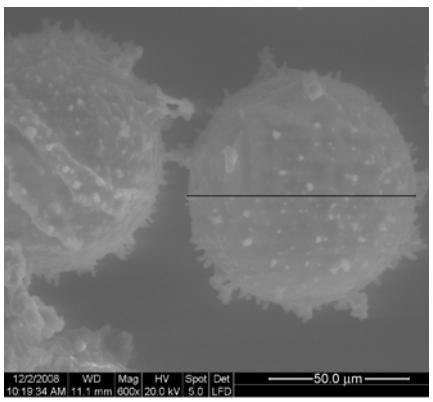

Figure 2 SEM micrographs: Size and shell morphology of microcapsules.

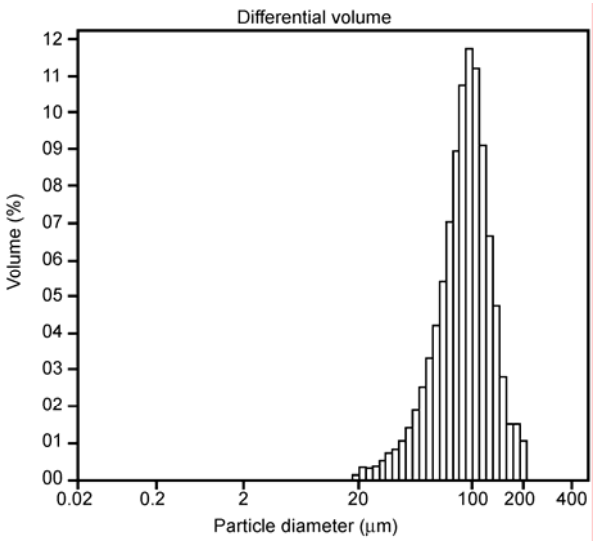

Figure 3 Particle size analysis of microcapsules.

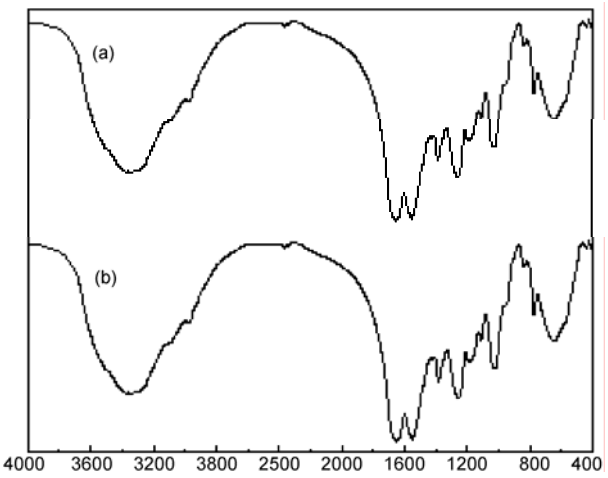

Figure 4 FTIR spectrums. (a) Shell material of microcapsule and (b) urea-formaldehyde resin.

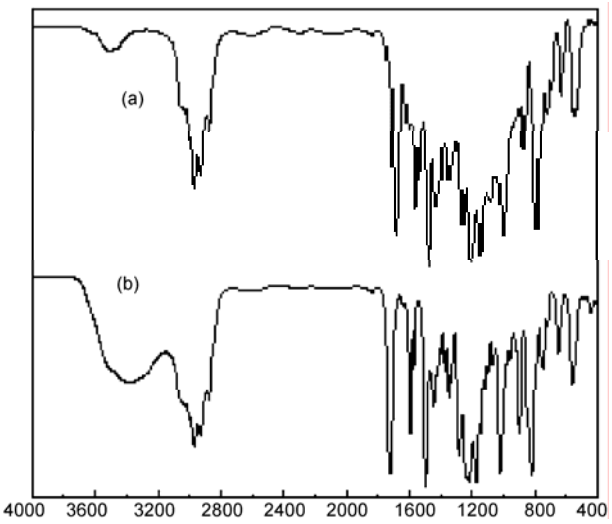

Figure 5 FTIR spectrum. (a) Core material and (b) microcapsule.

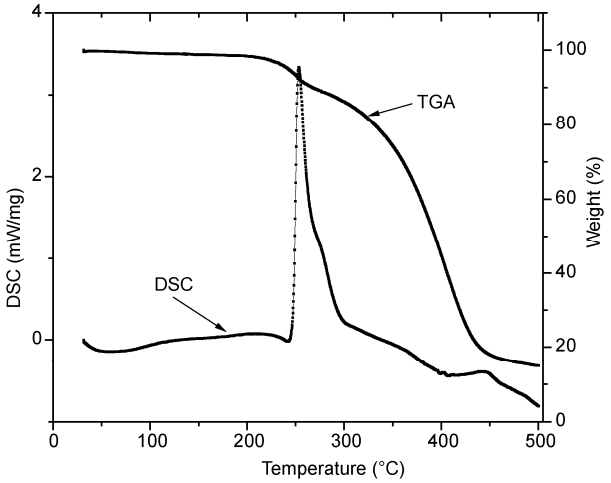

Figure 6 TG-DTA curve of microcapsules.

indicated that the weight between 30 and 200°C was mainly due to the removal of entrapped residual water and the elimination of free formaldehyde [20], it loss about 1.5%. The weight loss at temperatures between 200 and 250°C was mainly due to the decomposition of the PUF wall shell. Due to the formation and the higher thermal stability of cross-linked polymer yielded by the core material, the weight loss of microcapsules in the range of 250–450°C tends to increase and the slope of TGA curve becomes big. The residuals undergo extensive fragmentation above 450°C. Obviously, the microcapsules are chemically stable below 225°C, indicating that the prepared microcapsules have a good thermal stability.

2.4 Corrosion resistance of self-healing coating films

Corrosion of metallic substrate takes place when moisture and oxygen are transported through the cracks to the metal–coating interface. Healing of cracks, thus, provides an effective method to prevent corrosion. Performance of self-healing material was assessed by exposing specimens coated with paint containing filled microcapsules to salt spray. Before exposure, coated surface was cross-cut up to the metal. Control specimens had the paint without microcapsules. Up to 120 h of exposure, specimens with paint containing microcapsules were found free from corrosion at the scribed lines (Figure 7(a)). Control panels, however, suffered from corrosion after 48 h of exposure (Figure 7(b)). Superior corrosion resistance performance of healed films is due to the reason that, linseed oil released from ruptured microcapsules filled the crack and formed a film through oxidative polymerization with atmospheric oxygen which prevented the ingress of moisture and oxygen and thus prevented corrosion.

3 Conclusions

Microcapsules filled with epoxy resin 711 and E-51 by *in situ* polymerization of urea-formaldehyde in an oil-in-water emulsion were prepared successfully. In this study, the microcapsules have the rough outer surface composed of PUF nanoparticles. The PUF microcapsules filled with epoxy resin 711 and E-51 have good storage at room temperature and basically exhibit a good chemical stability below 225°C, which can withstand the moderate or high temperature processing of polymeric composites such as thermoset materials based on the epoxy resins.

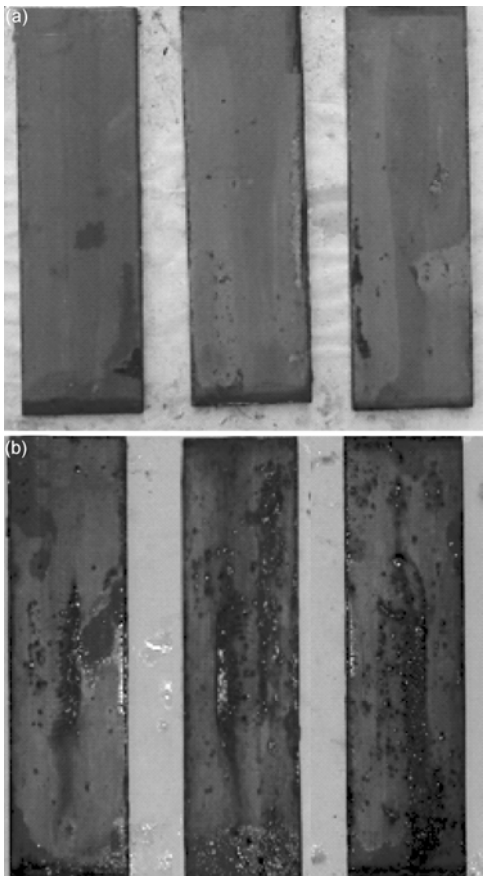

Figure 7 Salt spray performances of coatings (a) containing microcapsule (b) without microcapsule.

From the salt spray experiment of anticorrosion paint with microcapsules, the microcapsules in anticorrosion coatings released healing material, which healed cracks efficiently with satisfactory anticorrosive properties during cracking. In general, this research provides appropriate microcapsules for the self-healing composites and the self-healing performance of the microcapsule on the polymeric composites was examined in the study.

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