Synthesis and Characterization of Phenol–Formaldehyde Microcapsules Containing Linseed Oil and Its Use in Epoxy for Self-Healing and Anticorrosive Coating

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ABSTRACT: Phenol–formaldehyde microcapsules with linseed oil as an active agent were produced by applying *in situ* polymerization method. The anticorrosion and self-healing efficiency of the synthesized materials were studied. Characteristics of these synthesized capsules were studied by Fourier transform infrared spectroscopy, and surface morphology was analyzed by using scanning electron microscope. Controllable particle size was estimated at different rpm of stirrer and particle size was checked under microscope and also by using particle size analyzer. The anticorrosion performance of encapsulated microcapsules coated with epoxy resin was carried out in 5% NaCl aqueous solution. The effectiveness of linseed oil filled microcapsules was investigated for healing the cracks generated in paint films or coatings. It was found that the cracks were successfully healed when linseed oil was released from ruptured microcapsules. Further, linseed oil-healed area was found to prevent effectively the corrosion of the substrate in immersion studies. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 2911–2916, 2011

Key words: microencapsulation; phenol–formaldehyde (PF); self-healing; immersion studies

INTRODUCTION

Self-healing materials[1–5] represent a new paradigm for active and responsive materials. In a first-generation self-healing system,[6] the microencapsulated liquid healing agent, endodicyclopentadiene, and solid-phase Grubbs' catalyst are embedded in an epoxy matrix. When a microcrack propagates through the material, it ruptures the microcapsules and releases the healing agent into the damaged region, where it undergoes a polymerization on mixing with the catalyst phase. However, these conventional repair methods are not effective for healing invisible microcracks within the structure during its service life. Successful development of self-healing polymeric materials offers great opportunities for broadening the applications of these lightweight materials into the manufacture of structural and critical components. Encapsulation of functionally active materials in hollow microspheres is an attractive way of storing as well as protecting these from environment till required for fulfilling appropriate applications. Microencapsulated substances have been used for sustained drug release,[7] electro rheological fluids,[8] intumescent fire-retarding powders,[9,10] preservation of flavors, electrophoretic display applications, textiles and biotechnology,[11–17] etc. Self-healing polymeric materials have the built-in capability to substantially recover their load-transferring ability after damage. Such recovery can occur automatically or be activated after an application of a specific stimulus (e.g., heat, radiation). As such, these materials are expected to contribute greatly to the safety and durability of polymeric components without the high costs of active monitoring or external repair.

Recently, there has been growing interest in use of microencapsulated materials for healing of cracks generated during service of a polymer-based composite materials. Paints are extensively used for modification of substrates either for esthetic appearance or for corrosion protection. During its service life, the paint film undergoes changes in mechanical properties leading to 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. Throughout the development of this new range of smart materials, the mimicking of biological systems has been used as a source of inspiration.[18] One example of biomimetic healing is seen in the vascular-style bleeding of healing agents following the

Additional Supporting Information may be found in the online version of this article.

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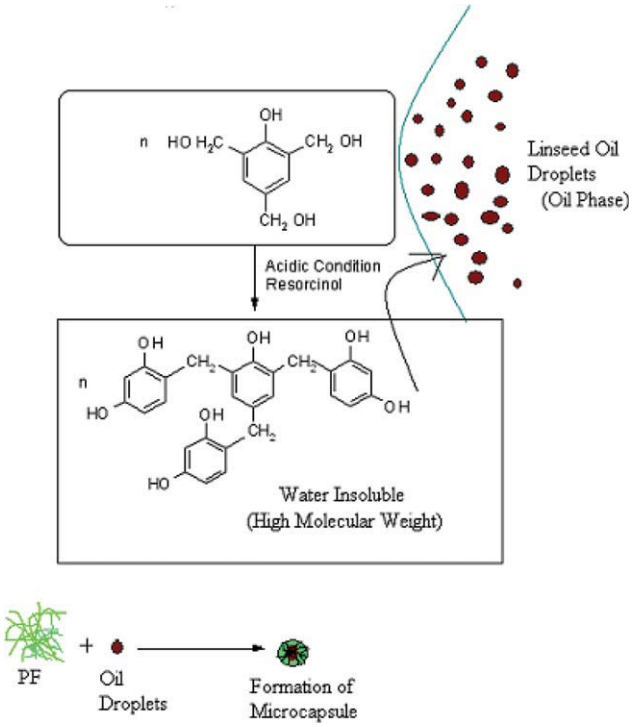

Figure 1 Reaction scheme for phenol–formaldehyde (PF) microcapsules production. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

original self-healing composites proposed by Dry and Sottos. These materials may also be able to heal damage caused by the insertion of other sensors/actuators, cracking due to manufacturing-induced residual stresses, and fiber debonding. In this work, we report the results of our investigations on the encapsulation of a linseed oil as a healing agent because of its film-forming ability by atmospheric oxidation. Linseed oil has a high content of unsaturated esters (oleic acid, linoleic acid, and α-linolenic acid) and is susceptible to polymerization reactions on exposure to oxygen in air. This polymerization results in the rigidification of the material, which gives the appearance of "drying." Microcapsules with phenol–formaldehyde (PF) as a shell and linseed oil as a core were synthesized by *in situ* polymerization (Fig. 1). Efficiency of these microcapsules in healing of cracks in an epoxy coating and corrosion protection has been estimated and further demonstrated by immersion studies.

EXPERIMENTAL

Materials

The materials used in experiments include phenol, formaldehyde, bisphenol (Loba Chemicals, Mumbai, India), xylene, resorcinol, epichlorohydrin, diethylene triamine (SD Fine Chemicals Ltd., Mumbai, India), and linseed oil (Calf Brand, Pune, India). All these chemicals were used as such in the experiment.

Synthesis of PF microcapsules

Microcapsules were prepared by following the process of *in situ* polymerization in an oil-in-water emulsion technique. Typically, 5 mL of 5 wt % aqueous solution of polyvinyl alcohol was mixed with 150 mL of distilled water in a three-necked flask. Under agitation, 3.76 g (0.04*M*) of phenol and 0.5 g of ammonium chloride were dissolved in solution. The pH of solution was adjusted to approximately 7 by using ammonia solution. Twenty-five milliliters of linseed oil containing 0.5 wt % cobalt octoate drier was added slowly to form an emulsion and allowed to stabilize for 30 min under agitation. After stabilization, 6.486 g (0.08*M*) of 37 wt % aqueous solution of formaldehyde was added. The reaction was started and slowly heated and maintained at 65 °C under stirring at 250 rpm for 2 h. Then, 5 wt % of HCl was added and the pH maintained at about 3; then, 0.5 g (0.0030*M*) of resorcinol was added, the reaction was monitored at the same temperature for about 2.5 h, and the reaction mixture was cooled to ambient temperature. Microcapsules from the suspension were recovered by filtration under vacuum. These microcapsules were rinsed with water, washed with xylene to remove suspended oil, and the capsules were dried under vacuum.

Synthesis of epoxy resin

Epoxy resin was synthesized by a method as reported in literature.[19]

Characterization

IR spectra of the samples were recorded on Fourier transform infrared spectroscopy (Perkin-Elmer Spectrum One 8400; Perkin-Elmer, Arlington, VA) as KBr pellets. The PF microcapsules were visualized by scanning electron microscopy (JEOL JSM 5400; Jeol, Akishima, Japan), where as surface morphology and capsule shell thickness were examined by (JEOL JSM 6360, Japan). Microcapsules were mounted on a conductive stage and ruptured with a razor blade to facilitate membrane thickness measurement, and particle size was analyzed by using laser particle size analyzer (Microtrac S3500; Microtrac, Inc., Montgomeryville, PA). Thermal decomposition was carried out using thermogravimetric analyzer (Shimadzu TGA 50; Shimadzu Corp., Tokyo, Japan) by heating the sample from room temperature to 600 °C at the heating rate of 10 °C/min under flowing nitrogen.

Linseed oil content in microcapsules

The quantity of linseed oil present in PF microcapsules was determined by extraction of oil using

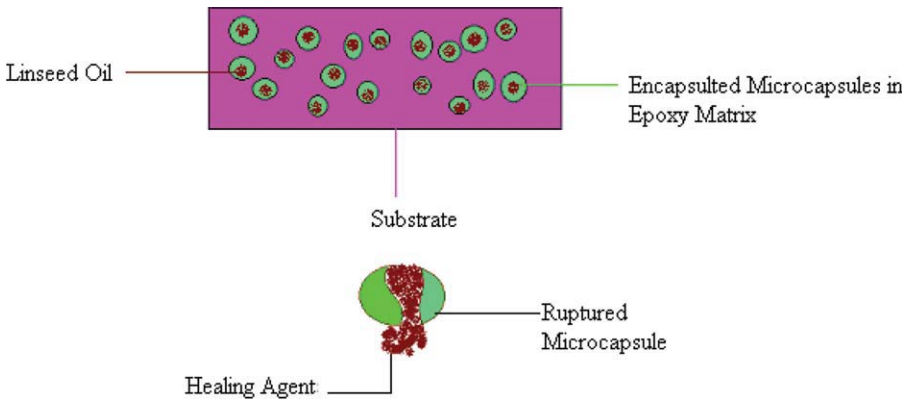

Figure 2 Schematic illustration of the dispersion of microcapsules in epoxy matrix and ruptured microcapsules with healing agent. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Soxhlet apparatus. A known weight of microcapsules (W_m) was transferred to a thimble, and extraction was carried out using xylene as a solvent. After 2 h of extraction, thimble was carefully taken out from Soxhlet apparatus, and, after completely wearing the solvent, it was dried in oven for 12 h. The final weight of the shells (W_s) was noted. The quantity of linseed oil was determined with the help of the following equation.

$$\text{Weight of linseed oil } (\%) = \frac{W_m - W_s}{W_m} \times 100$$

Evaluation of self-healing process

The self-healing function of these microcapsules on a glass substrate surface was evaluated by incorporating microcapsules into a 10 wt % solution of epoxy in xylene with hardener. Colored linseed oil-filled microcapsules were mixed in epoxy solution to produce contrast in the crack when observed under optical microscope to record the healing process (Fig. 2). A glass substrate of dimension 80 mm × 25 mm × 1 mm was coated with the above mixture as a single coat to produce a dry film having thickness of about 150 μm. After 7 days of curing, a crack was created in the coated glass substrate by using razor blade; the scribe depth was uniform within ~10 μm. Glass plate was immediately held under objective lens of optical microscope (40×) to record healing process initiated because of release of linseed oil from ruptured microcapsules until completion of healing.

Immersion studies

The synthesized PF microcapsules were used for the preparation of PF/epoxy coatings. The PF/epoxy coatings were prepared separately, by dispersing PF microcapsules in 10 wt % solution of epoxy in xylene with hardener. The coatings were applied by brush on all sides of the steel strips of dimension (150 mm × 100 mm × 1 mm) having thickness ≈150 μm. The self-healing anticorrosion function of this coating system was evaluated through immersion studies of damaged and healed microcapsules coated steel samples by comparing with steel samples without microcapsules. Damage was induced by hand scribing using a razor blade, and, after the scribing, the samples were allowed to heal at room temperature for 24 h. Immersion studies of these coatings were carried out with home-made equipment.[20] The samples were tested for a total exposure time of 72 h. The corrosion of the damaged area was monitored by visual inspection using digital camera (Olympus FE-25).

RESULTS AND DISCUSSION

Fourier transform infrared spectroscopy analysis

In case of PF resin (Fig. S1, Supporting information), the transmissions peaks observed at 1680 and 1462 cm^{-1} are attributed to the C=C aromatic ring vibrations, the peaks at 1250 and 1154 cm^{-1} are characterized to the C—C—O asymmetric stretch, and C—H in plane deformations, respectively. The 980 and 748 cm^{-1} peaks belonged to the C—H out of plane vibrations. The peak at 1370 cm^{-1}, which corresponded to the phenolic O—H in plane bend, was also detected for PF resin.[21] However, for linseed oil (Fig. S2, Supporting information), the main stretching absorptions were observed for ester C=O (1745 cm^{-1}), aliphatic C=C (1696 and 1548 cm^{-1}), and ester C—O (1384 and 1278 cm^{-1}), respectively.

Surface morphology

The surface morphology of microcapsules synthesized under various agitation rates was observed using microscope (40× and 100×), and the results

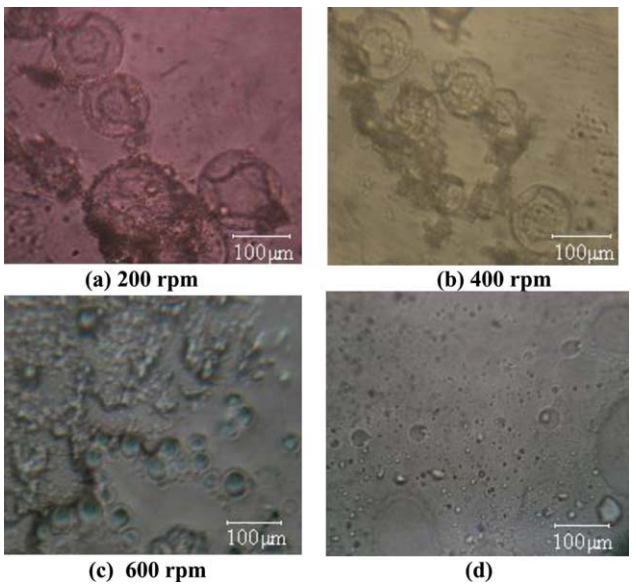

Figure 3 PF microcapsules obtained at various agitation rates. (a) 200 rpm, (b) 400 rpm, (c) 600 rpm, and (d) PF microcapsules in epoxy resin. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

are presented in Figure 3. The spherical microcapsules were obtained at all agitation rates. In this study, we realized that the outer surface of the capsules was relatively smooth, with some wrinkling because of the interaction of inhomogeneous reaction kinetics, fluid-induced shear forces, and shell-determined elastic forces.[22] The inner surface is generally smoother because little shear flow occurs inside the capsule during the formation of the shell wall. At low agitation rates (200–400 rpm), the obtained microcapsules were relatively large in the range 100–150 μm [Fig. 3(a,b)]. This is an important finding of this study under reported conditions and may be because of the reason that the specific interface area would be reduced and more polymerized product formed at interface. At higher shear rates (600 rpm), the microcapsules with average diameter of 50–60 μm were obtained, and their shell wall was found to be more uniform [Fig. 3(c)], which might be because of increased interfacial area and more homogeneous reaction. At low agitation rate, interfacial tension dominates and dispersed droplets remain large. Large droplets are broken up into small ones when strong shear forces are experienced under high agitation rate. On incorporation of microcapsules into epoxy matrix, it was found that microcapsules could be uniformly mixed without any damage into epoxy by stirring at 200 rpm for 20 min [Fig. 3(d)]. Figure 4 visualizes the scanning electron microscopy micrographs of PF microcapsules at 400 rpm [Fig. 4(a)], 600 rpm [Fig. 4(b)], ruptured microcapsule with linseed oil [Fig. 4(c)], surface morphology [Fig. 4(d)], and capsule shell thickness [Fig. 4(e)].

Particle size analysis

Figure 5 shows the particle size distribution of the prepared PF microcapsules containing linseed oil. The microcapsules' size ranges from 10 to 150 μm, and the mean diameter is 70 μm. It is observed that the microcapsules' size can be controlled by controlling the rate of agitation. The flow of fluid is turbulent around the stirrer blade, and, therefore, many smaller microcapsules are generated in the vicinity of stirrer blade, whereas microcapsules take their shape larger in the region of flow away from the blade.

Thermogravimetric analysis

The thermograms of PF microcapsules with linseed oil and PF shell are shown in Figure 6. In case of PF shells, the thermogram showed one-stage degradation that started at 335.39 °C and continued upto 567.61 °C. This was attributed to the degradation of PF resin with a total weight loss of 91.41% after 567.61 °C. For PF microcapsules, initial decomposition started at 208.66 °C and continued up to 317.91 °C because of decomposition of linseed oil from the microcapsules. The second-stage weight

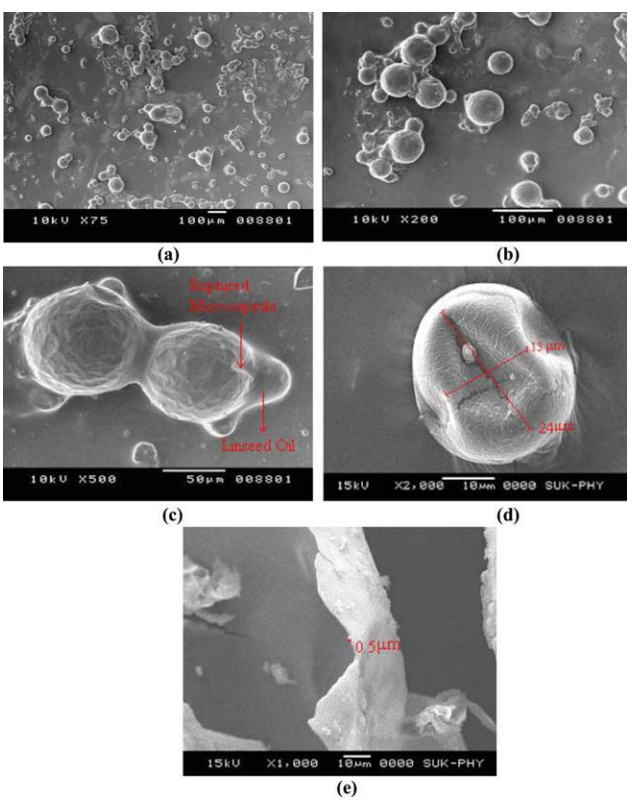

Figure 4 Scanning electron microscope micrographs. (a) PF microcapsules at 400 rpm. (b) PF microcapsules at 600 rpm. (c) Ruptured microcapsule with linseed oil. (d) Surface morphology of PF microcapsule. (e) Shell thickness. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

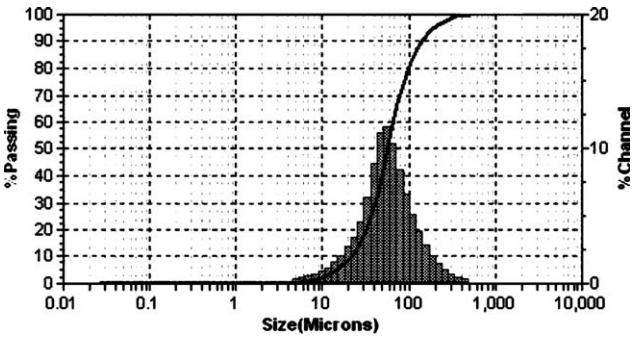

Figure 5 Particle size histogram of PF microcapsules.

loss started from 370.78 °C, corresponding to the decomposition of shell material, and total weight loss was about 98.10% after 571.56 °C. In general, from thermogravimetric analysis, it was concluded that weight loss is much more in PF microcapsules compared with PF shell. It clearly indicated that microcapsules contain materials, i.e., linseed oil (as core) and PF resin (as a shell).

Healing performance

The PF microcapsules with linseed oil play an important role to seal the coating. Microcapsules should break immediately to release healing material when the cracks are generated in the epoxy coating [Fig. 7(a)]. The released linseed oil goes through the crack and slowly repair the coating [Fig. 7(b,c)] and fill the maximum crack within 180 s [Fig. 7(d)]. The amount of linseed oil encapsulated in PF microcapsules was determined using Soxhlet apparatus and was found to be 78%. Hence, the maximum amount of linseed oil in PF microcapsules plays an important role in self-healing coating. Linseed oil has the ability of oxidation with atmospheric oxygen and, thus, to seal the crack in the coating.

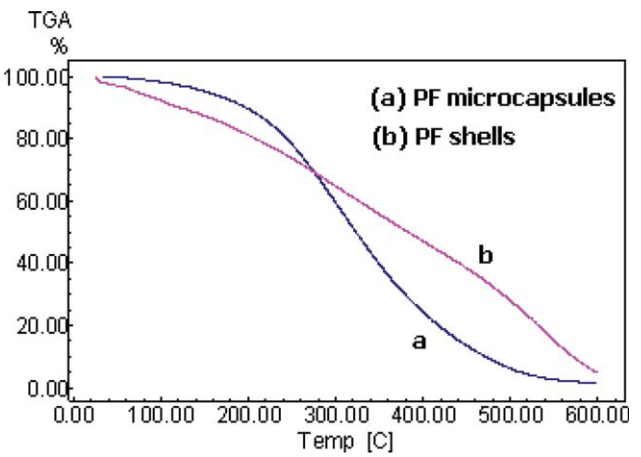

Figure 6 Thermogravimetric analysis curves of (a) PF microcapsules and (b) PF shells. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

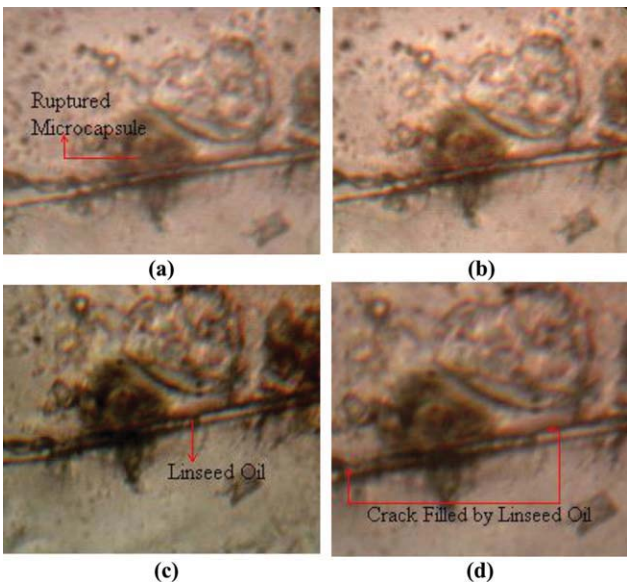

Figure 7 Optical microscope photos of self-healing coating films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Immersion studies

The corrosion and rust formation on carbon steel involves several steps of oxidation and reduction processes as given below.

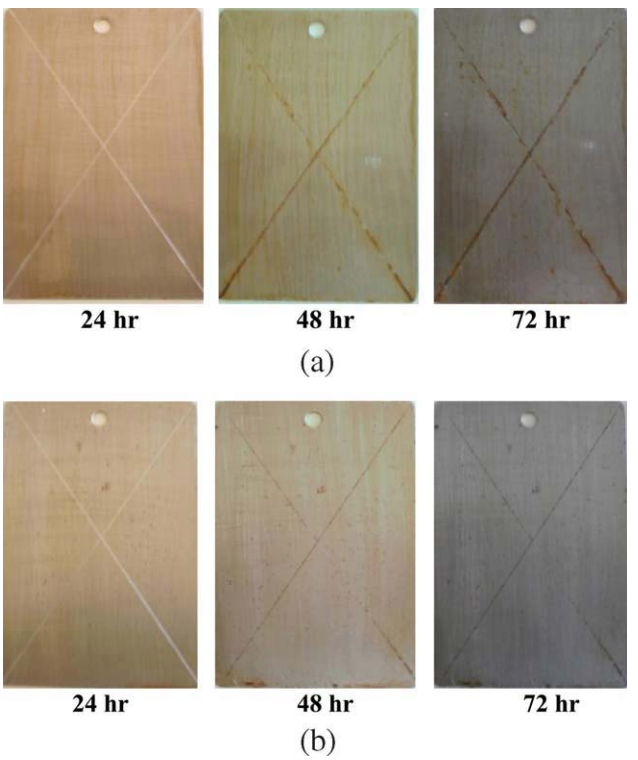

Figure 8 Immersion studies performance of (a) without and (b) with microcapsules coatings at different exposure periods. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$Fe \rightarrow Fe^{2+} + 2e^{-} \quad \text{(i)}$$

$$Fe^{2+} \rightarrow Fe^{3+} + 1^{e-} \quad \text{(ii)}$$

$$O_2(g) + 2H_2O + 4^{e-} \rightarrow 4OH^{-} \quad \text{(iii)}$$

$$2Fe^{2+}(aq) + O_2(g) + 2H_2O \rightarrow 2FeOOH + 2H^{+} \quad \text{(iv)}$$

If any of these processes are under arrest, the corrosion is inhibited, and the coating becomes helpful for corrosion prevention. It has been seen that healing of cracks, thus, provides an effective method to prevent corrosion. Before immersion studies, coated surface was crosscut up to the metal. Figure 8(a) shows the coating without microcapsules. The specimens with microcapsules were found to be free from corrosion and blister at the scribed lines after 72 h of immersion studies [Fig. 8(b)]. However, specimens without microcapsules rapidly corrode within 48 h and exhibited extensive rust formation, most prevalently within the groove of the scribed regions, and also extending rusting across the substrate surface. 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 by oxidative polymerization with atmospheric oxygen. The above reactions steps (i) to (iv) were found to be prevented by the presence of linseed oil in the microcapsules, which improves tremendously the barrier properties of coating as well as self-healing effect and, thus, gives large advantage in anticorrosion behavior.

CONCLUSION

PF has been successfully used as an encapsulating material for linseed oil. The microcapsule size has been effectively controlled by stirring rate. The smoothness of these microcapsules enhances the bursting during development of cracks in the paint coating. The linseed oil inside the microcapsules acts as a healing material and heals the cracks efficiently by oxidation; furthermore, it also acts as an anticorrosive agent on the surface of the matrix.

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