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Synthesis of multicore phenol formaldehyde microcapsules and their application in polyurethane paint formulation for self-healing anticorrosive coating

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Abstract

Background: This paper describes the microencapsulation of linseed oil along with drier and corrosion inhibitor in polyurethane coating.

Results: Linseed oil along with drier and corrosion inhibitor was encapsulated in phenol formaldehyde microcapsules successfully by *in situ* polymerization process. These microcapsules were characterized by Fourier transform-infrared and nuclear magnetic resonance spectroscopies, and their surface morphology was studied by scanning electron microscopy. The particle size of the prepared microcapsules was estimated by optical microscopy and confirmed using a particle size analyzer. The self-healing properties as well as anticorrosive performance of encapsulated microcapsules were studied in polyurethane coating. Corrosion protection of coatings with microcapsules containing linseed oil, corrosion inhibitor, and drier was compared with pristine coating free from microcapsules.

Conclusions: The cracks in the paint film could be successfully repaired by the release of linseed oil from microcapsules ruptured under stimulated mechanical action, while corrosion inhibitor plays an important role to prevent the corrosion in a scribed line region.

Keywords: Self-healing, Phenol formaldehyde, Microcapsules, Linseed oil, Anticorrosive performance, Polyurethane coating, Corrosion inhibitor

Background

Self-healing materials encapsulated in polymeric backbone represent a new research area for functional materials in paints and coatings. Microencapsulation techniques can be utilized to encapsulate a range of substances of different phases such as gasses, liquid, and solids. Depending upon the substance with required characteristics to be encapsulated, one can develop a technology which can have multiple applications [1,2]. Several functional materials have been encapsulated [3-5] for various applications like sustained drug release [6], electrorheological fluids [7], intumescent fire-retarding powders [8-10], preservation of flavors, electrophoretic displays, textiles, and biotechnology [11-15]. Self-healing polymeric materials have built-in ability to fill the microcracks developed during mechanical action [16,17], which can occur autonomously or be activated after an application of a specific stimulus (e.g., heat, radiation).

Paints are extensively used on various substrates for aesthetics as well as for protection in their service life period. In the case of paints used for protection in a corrosive atmosphere, the coating film undergoes changes in surface morphology, leading to the formation of microcracks which subsequently propagate and expose substrate to atmospheric moisture and oxygen [17]. In our previous

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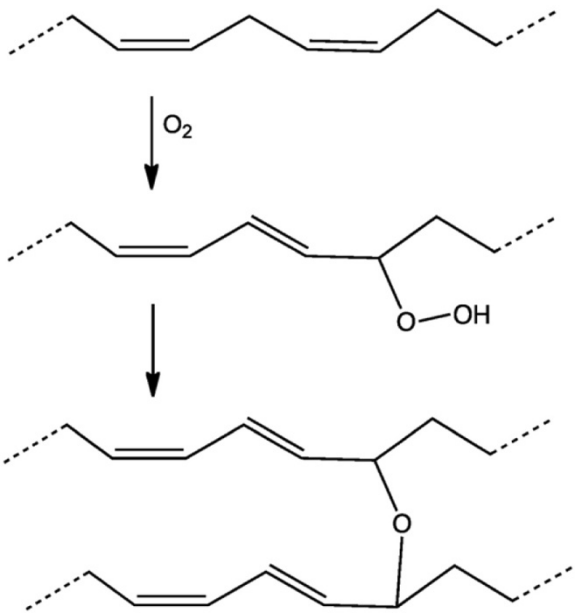
work, we have demonstrated how these microcracks, if healed, can help in regaining the anticorrosive performance. This was achieved by the healing efficiency of epoxy coating using phenolformaldehyde (PF) microcapsules containing linseed oil and drier [16].

In this work, we report the microencapsulation of linseed oil along with drier and corrosion inhibitor in polyurethane coating. Linseed oil due to its high content of unsaturated esters of oleic acid, linoleic acid, and linolenic acid is susceptible to polymerization reactions upon exposure to oxygen in air. This polymerization results in the rigidification of the material, protecting the metal from corrosive species. The schematic representation of the mechanism of drying oil is shown in Scheme 1. Microcapsules having PF as shell and linseed oil, drier, and corrosion inhibitor as core were synthesized by *in situ* polymerization. The schematic representation of this *in situ* polymerization is shown in Scheme 2. The efficiency of these microcapsules in healing cracks in polyurethane coating and corrosion protection has been studied and further demonstrated.

Methods

Characterization

Infrared (IR) spectra of the samples were recorded on KBr pellets using a Fourier transform-infrared (FTIR) spectrometer (Perkin Elmer Spectrum One, 8400, PerkinElmer, Waltham, MA, USA). Nuclear magnetic resonance (NMR) spectra of the samples were recorded on Bruker 300 MHz (Bruker AXS, Inc., Madison, WI, USA) in $CDCl_3$. The PF microcapsules were visualized using an optical microscope, whereas the surface morphology and capsule shell thickness were examined using a scanning electron microscope (SEM; JEOL JSM 6360, JEOL Ltd., Akishima-shi, Japan). Microcapsules were mounted on a conductive stage and ruptured with a razor blade to facilitate membrane thickness measurement. The particle size was analyzed using a laser particle size analyzer (Microtrac X 100, Microtrac, Largo, FL, USA). The coating thickness was measured using a digital meter (Positector, DeFelsko, Ogdensburg, NY, USA). Immersion studies of the coatings were carried out in 5% NaCl solution. The sample panels were tested for a total exposure time of 480 h. The corrosion of the damaged area was monitored by visual inspection using a digital camera (Olympus FE-25, 10 megapixels, Olympus Corporation, Shinjuku, Tokyo, Japan).



Scheme 1 Reaction mechanism of drying oil.

Quantity of core material present in microcapsules

The percentage of core material present in PF microcapsules was determined by the extraction of core material using the 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 the Soxhlet apparatus and dried in an oven at 80°C to 85°C for 12 h. The final weight of the shells (W_s) was noted. The quantity of linseed oil was determined with the help of following equation [16]:

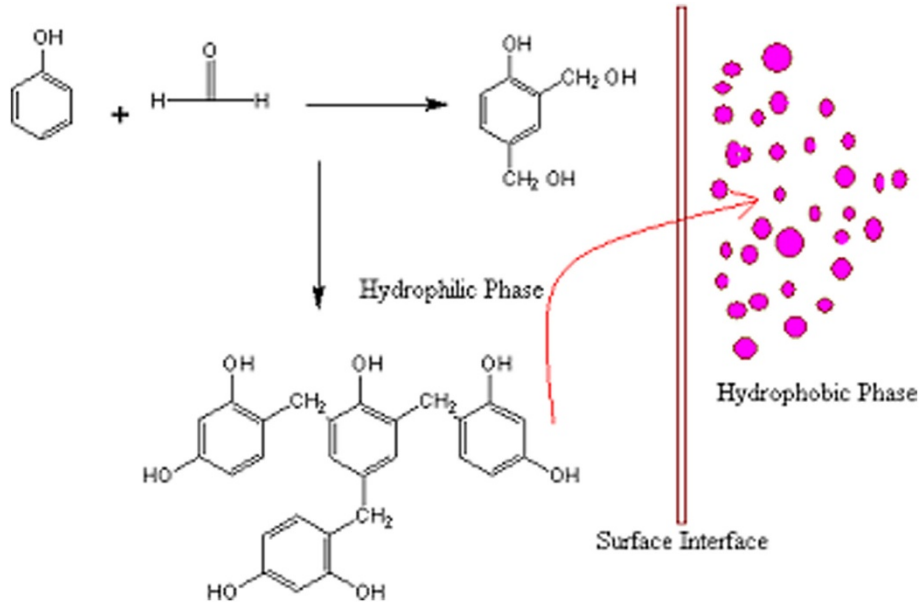
$$\text{Percentage of core material } (\%) = \frac{W_m - W_s}{W_m} \times 100$$

Controlled release study

Controlled release behavior of phenol formaldehyde microcapsules containing dual core and multicore was investigated using the loss after drying method. In this method, 0.1 g of microcapsules was transferred into dry Gooch crucible with stop cork followed by the addition of 10 mL of xylene with gentle stirring at room temperature. The microcapsules were kept in contact with xylene for extraction over a period of 60 min, and then, the eluent containing the core material was collected by opening the stop cork. This process was repeated at 2-h interval, and all the core materials were extracted.

Self-healing and anticorrosion studies

The PF microcapsules were used for the preparation of PU self-healing coatings. The PU coatings were prepared by dispersing 2 wt.% of PF microcapsules in PU clear as well as white paint formulations. The PU clear coatings were applied by dip coating method on a glass slide with the size of 20 mm × 50 mm × 2 mm having a dry film thickness (DFT) of about 50 μm, while the coatings of



Scheme 2 Reaction for phenolformaldehyde (PF) microcapsule production.

the white paint were applied using a conventional spray gun on steel strips with the dimension of 150 mm × 100 mm × 1 mm having a DFT of about 100 μm. The self-healing of PU clear coating containing microcapsules was demonstrated using an optical microscope. The self-healing and anticorrosion function of PU paint film were evaluated through immersion studies of coated steel samples by comparing with steel samples without microcapsule as a control. Damage was induced by scribing a cross-cut through a razor blade having a cut thickness of about 10 μm, and after scribing, the samples were allowed to heal at room temperature for 24 h.

Results and discussion

FTIR and NMR analysis

The core material extracted as explained in the 'Quantity of core material present in microcapsules' section was used for FTIR and NMR analysis. In the case of FTIR spectroscopic analysis for PF shell (Figure 1a), the absorption bands observed at 1,696 and 1,462 cm^{-1} were attributed to the C=C aromatic ring vibrations, and the bands at 1,274 and 1,154 cm^{-1} were characterized to the C-C-O asymmetric stretching and C-H in plane deformations, respectively. The bands at 980 and 719 cm^{-1} belonged to the C-H out of plane vibrations. The band at 1,384 cm^{-1} corresponding to the phenolic O-H in plane bending was also detected for PF resin [18,19]. However, for linseed oil (Figure 1b), the main stretching absorption bands were observed for ester C=O (1,745 cm^{-1}), aliphatic C=C (1,696 and 1,548 cm^{-1}), and ester C-O (1,384 and 1,278 cm^{-1}) groups. For core A (linseed oil/drier/Alcophor AC) (Figure 1c), the same absorption bands were observed as compared to linseed oil. Finally, for the confirmation of corrosion inhibitor in core A sample, additional information was collected from ^{1}H NMR spectral analysis of core A (Figure 1d) and linseed oil (Figure 1e) samples separately. In the NMR spectra, some extra multiplets were observed for core A sample in the range of δ 0.56 to 2.45 ppm due to the presence of aliphatic protons (δ 0.86 ppm) and also for -OCH_3 (δ 2.10 ppm) present in Alcophor AC [20,21]. The multiplets at δ 4.95 to 5.56 ppm and δ 7.12 to 7.45 ppm were observed for aliphatic -OH groups and aromatic -OH groups, respectively, present in tannin (polyphenolic compound). The NMR study has confirmed thatcore A contained analkoxy-modified tannin compound, i.e., Alcophor AC.

Effect of the rate of agitation during the synthesis of microcapsules

The PF microcapsules were synthesized at different agitation rates and observed using an optical microscope. The obtained results are depicted in Figure 2, which clearly show that spherical microcapsules were obtained at all agitation rates. At low agitation rate (200 rpm), the microcapsules obtained were comparatively large having the diameter of 100 to 120 μm (Figure 2a). At 300 to 400 rpm, the microcapsules with reduced size with average diameter in the range of 40 to 50 μm were obtained (Figure 2b,c). The sizes of microcapsules synthesized at 500 rpm were found to be in the range of 20 to 40 μm (Figure 2d). These might be due to increased interfacial area and more homogeneous reaction occurring at the microcapsule surface with increase in agitation rates. It

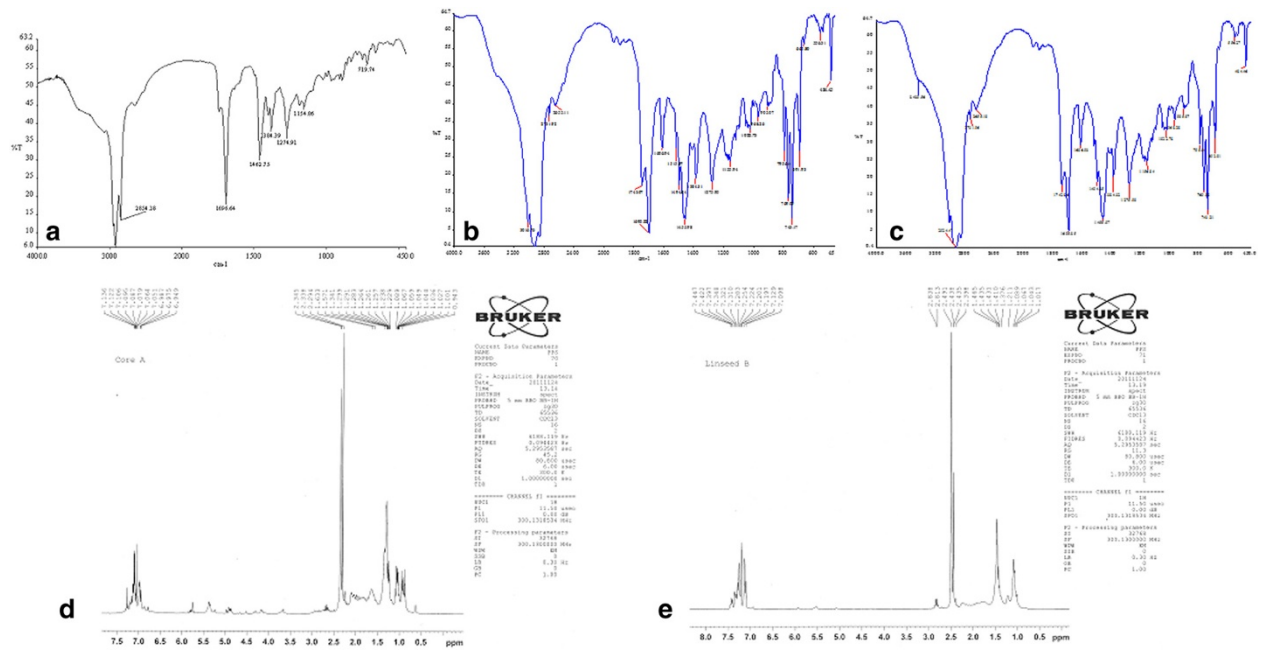


Figure 1 IR and NMR spectra. (**a**) IR spectra of PF shell. (**b**) IR spectra of linseed oil. (**c**) IR spectra of linseed oil and corrosion inhibitor (core A). (**d**) NMR spectra of core A containing the mixture of linseed oil and Alcophor AC. (**e**) NMR spectra of linseed oil.

means that a high agitation rate (≥500 rpm) producesa dispersion force which might be sufficient to breakdown the large oil droplets into smaller ones and can uniformly disperse the tiny oil droplets into the emulsion [22].

SEM analysis

The SEM micrographs further supported that PF microcapsules are spherical and round in shape with awrinkle-free surface morphology. The particle size of microcapsules synthesized at 500 rpm was found to be 20 to 40 μm (Figure 3a). Surface morphology of a single PF microcapsule clearly showed the smooth and even surface of microcapsules (Figure 3b). The microcapsules were ruptured to measure the shell thickness, and it was found to be 0.4 to 0.5 μm (Figure 3c). During the formation of PF microcapsules, resorcinol plays an important role to combine and crosslink phenol formaldehyde oligomers, leading to the formation of a

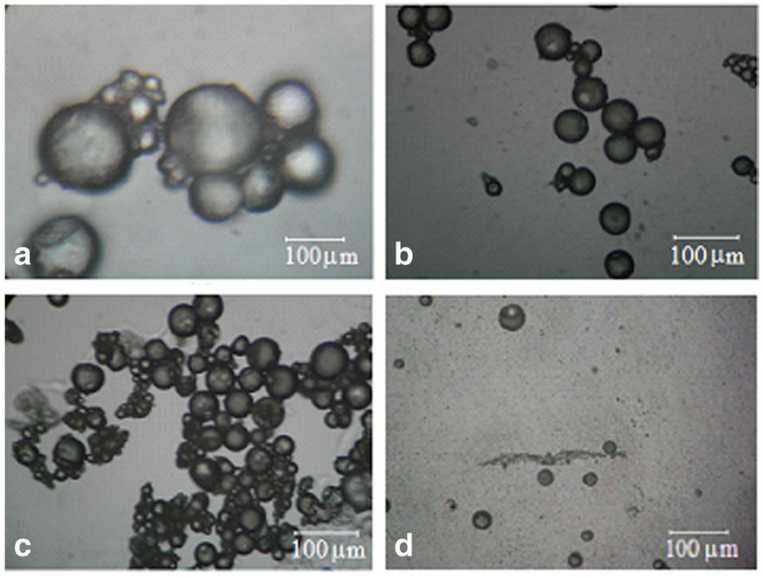


Figure 2 PF/linseed/Alcophor AC microcapsules obtained at various agitation rates. (**a**) 200, (**b**) 300, (**c**) 400, and (**d**) 500 rpm.

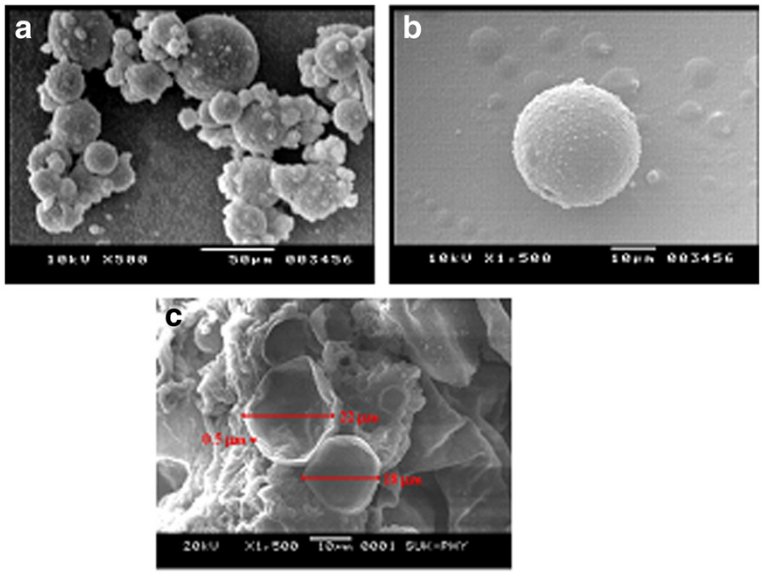


Figure 3 SEM micrographs. (**a**) PF/linseed/Alcophor AC microcapsules at 500 rpm, (**b**) surface morphology of microcapsule, and (**c**) ruptured shells with thickness.

tough protective uniform shell for the active core material.

Particle size analysis and determination of the volume of the core

The observed results of the particle size distribution of the PF microcapsules are shown in (Figure 4a). In the particle size histogram of PF microcapsules, the overall size ranged between 5 and 100 μm, and the mean particle size obtained was ±30 μm. The circumference and volume of each individual microcapsule and core material present in it can be easily calculated, as depicted in Figure 4b, by $2\pi r$ and $4/3\pi r'^3$ equations, where r is the radius of microcapsule, h is the shell thickness, and r' is the radius of core which is equal to $r–h$. In a mean particle size of 30 μm having a shell thickness equal to 0.5 μm, the circumference of microcapsules calculated was 94.2 μm and the circumference of core material was 91.06 μm. The volume of active core material present in the mean particle size of the microcapsule has been estimated as 12,731.66 μm^3.

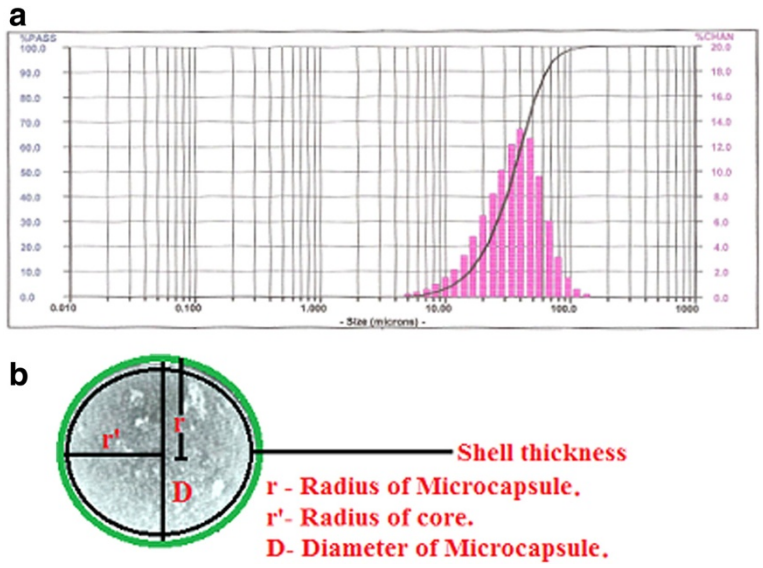


Figure 4 (a) Particle size histogram of PF/linseed/Alcophor AC microcapsules, (b) calculation of volume of active core material.

Table 1 Quantitative analysis of core material released from PF/linseed and PF/multicore microcapsules

Time (h)	Core released of PF/ linseed oil/Alcophor AC microcapsules (%)	Core released of PF/ linseed oil microcapsules (%)
0	0	0
2	11.88	11.3
4	56.43	55.9
6	77.22	76.78
8	85.14	85.11

Quantity of core material present in microcapsules and controlled release study

The amount of dual and multicore encapsulated in PF microcapsules was determined using the Soxhlet apparatus and calculated as described in the 'Quantity of core material present in microcapsules' section. About 85% of core material was found to be present in both microcapsules. The results were confirmed in controlled release study as per the procedure described in the 'Controlled release study' section. The percentage of core material released slowly from both microcapsules is summarized in Table 1. About 85% core material was collected in 8 h from both microcapsules. This controlled release of core material would be useful in the efficient healing ability of the damaged coating and for better corrosion protection.

Self-healing and anticorrosion studies

In our previous work, it has been established that linseed oil and drier present in PF microcapsules play a vital role, providing a successful method to heal the cracks and inhibit the corrosion process in epoxy coating [16]. The role of linseed oil, drier,and corrosion inhibitor present in PF microcapsules for healing of PU coatings is reported here. The evaluation of self-healing and anticorrosive properties of the synthesized PF microcapsules were carried out as described in the 'Self-healing and anticorrosion studies' section.

The damage to the coating was induced by scribing a crosscut through a razor blade having a cut thickness of about 10 μm, and after scribing, the samples were allowed to heal at room temperature for 24 h. First, the PU clear coatings with and without multicore PF microcapsules were observed under an optical microscope to determine the healing action of microcapsules. The images in Figure 5a,b clearly depict the self-healing ability of coating containing PF microcapsules. In the case of coating without PF microcapsule, the scribed portion appears to be hollow devoid of any material, whereas the scribed part of the coating containing PF multicore microcapsules appears as black deposition comprising of filled core material released from ruptured microcapsules. The images also depict the presence of smooth and spherical PF microcapsules dispersed in the coating portion which was not scribed.

The self-healing ability was further confirmed by evaluating PU paint-coated panel with and without microcapsules by immersion studies. It was observed that the PU paint-coated panel without microcapsules quickly corroded within 120 h of immersion in 5% salt solution (Figure 6a). However, the PU-coated panels with dual core as well as multicore microcapsules were found to be free from corrosion, rust, and blisters at the scribed lines of crosscut after 120 h of immersion studies (Figure 6b,c). In addition, it was interesting to note the healing of cracks in the crosscut part of coating containing microcapsules. The extent of healing was found to be higher for multicore as compared to dual core.

In the further study, after 120 h of immersion, on these same three panels, the numbers of horizontal cuts were made, and self-healing efficiency was evaluated for another 480 h of immersion studies. The panel without microcapsules showed extensive rust formation, blisters most readily within the groove of the scribed area, and also extending rusting, blistering across the substrate surface (Figure 7a). The panels with dual-core microcapsules exhibited better corrosion resistance (Figure 7b). The anticorrosive performance is due to the healing

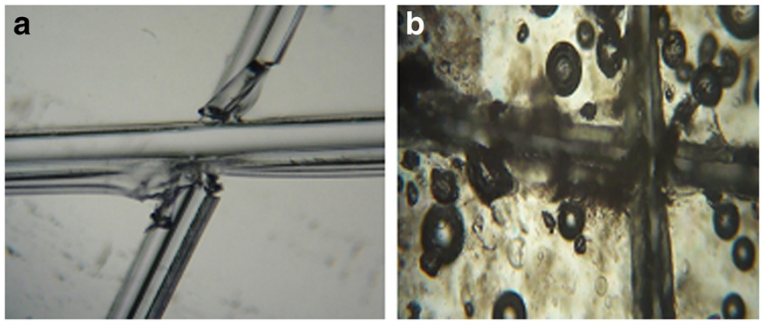


Figure 5 Self-healing ability of the coating - (a) clear coating and (b) coating with microcapsules.

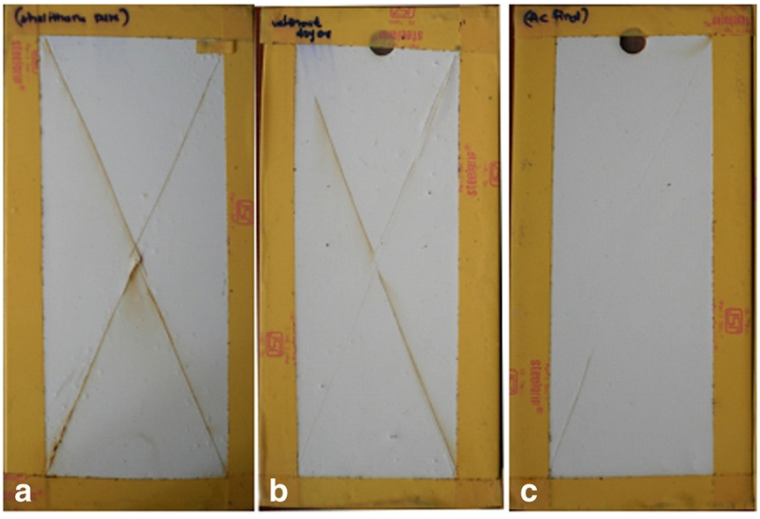


Figure 6 Crosscut panels after 120-h immersion studies. (**a**) Pristine PU coating, (**b**) coating with PF/linseed/drier microcapsules, and (**c**) coating with PF/linseed/drier/corrosion inhibitor microcapsules.

induced by linseed oil released from ruptured microcapsules, filling the cracks and forming a film by oxidative polymerization with atmospheric oxygen. The panels with PF multicore microcapsules showed even better corrosion protection as compared to the other two coatings with most of the cracks in the coating being healed as well as prevented from the corrosion formation in the scribed line region (Figure 7c). The presence of corrosion inhibitor in the multicore microcapsules has played an additional role in the protection against corrosion.

Experimental

Materials

The materials used in the experiments include linseed oil (Calf Brand, Pune, India), phenol, 37% formaldehyde solution, resorcinol, xylene, ammonium hydroxide, ammonium chloride, hydrochloric acid and polyvinyl alcohol (SD Fine Chemicals Ltd., Mumbai, India), Shalithane XL HB Finish White - a two-pack polyurethane (PU) paint containing base and accelerator and Shalithane XL HB Finish Clear - a two-pack PU clear coating containing base

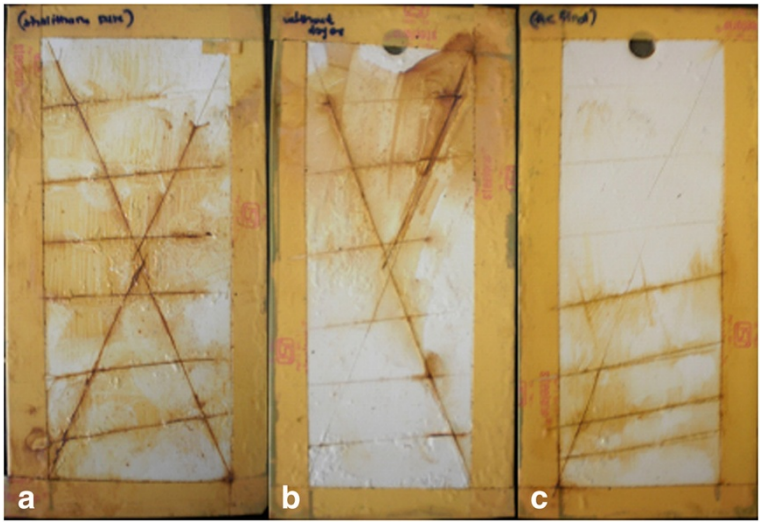


Figure 7 Crosscut panels after 480-himmersion studies. (**a**) Pristine polyurethane coating, (**b**) coating with PF/linseed microcapsules, and (**c**) coatings with PF/linseed/Alcophor AC microcapsules.

and accelerator (Shalimar Paints Ltd., Mumbai, India), and Alcophor AC - an alkoxy-modified tannin compound used as corrosion inhibitor (Cognis, Monheim, Germany). All these chemicals were used as such without any further purification in the experiments.

Synthesis of PF microcapsules

Microcapsules were prepared by *in situ* polymerization by 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 of phenol and 0.5 g of ammonium chloride were dissolved in solution. The pH of the solution was adjusted to approximately 7 to 8 using an ammonia solution. Then, 25 mL of linseed oil containing 0.5 wt.% of cobalt naphthenate drier (dual core) or 25 mL of linseed oil containing 0.5 wt.% cobalt naphthenate drier with 5 mL of 50 wt.% of Alcophor AC solution in xylene (multicore; AC Solutions, Fairbanks, AK, USA) was added slowly to form an emulsion and allowed to stabilize for 30 min under agitation. After stabilization, 6.486 g of 37% formaldehyde solution was added slowly under agitation. The temperature was raised slowly and maintained at 65°C under stirring at 250 rpm for 2 h, leading to the formation of microcapsules with PF polymer as shell and multicore materials comprising of linseed oil, drier, and corrosion inhibitor. To strengthen the shell, the PF polymer was further crosslinked by adding 5 wt.% of HCl maintaining the pH at about 3 followed by the addition of 0.5 g of resorcinol. The reaction mixture was stirred at 65°C for about 2.5 h, and then, the reaction mixture was cooled to ambient temperature. Microcapsules from the suspension were recovered by filtration under vacuum, rinsed with water, washed with xylene to remove suspended oil, and then dried under vacuum.

Conclusions

The linseed oil along with dried and corrosion inhibitor was successfully microencapsulated in phenol formaldehyde microcapsules.

1. Phenol formaldehyde was found to be an effective encapsulating material for linseed oil, drier, and corrosion inhibitor.
2. The microcapsule size could be effectively controlled by agitation (stirring) rate.
3. The rough or tough surface morphology of the microcapsules provides good anchorage between the coating matrix and the substrate.
4. The multicore material inside the PF microcapsules used as a healing material remains intact on coating till it is required for crack filling application (self-healing application).
5. Corrosion inhibitor along with linseed oil prevents corrosion in scribed line region.
6. Linseed oil heals the cracks efficiently by oxidation and cures the mechanical cracks developed during stresses; furthermore, it also acts as an anticorrosive agent on the surface of the matrix.

The present investigation could be useful for further research to minimize the problems of metal corrosion through self-healing process.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

RSJ participated in paint formulation experiments for this research project, AVB participated in polymer synthesis experiments for this research project, VM participated in paint characterization, DGH guided in the polymer synthesis, PPM guided in the polymer synthesis and inference of spectroscopic analysis, and GW guided in paint formulation and characterization. All authors read and approved the final manuscript.

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