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Tung Oil-Urea Formaldehyde Microcapsules for Anti-Corrosive Self-Healing Epoxy Coatings

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Abstract

Self-healing coating was developed using Tung oil as a self-healing agent, encapsulated in urea-formaldehyde (UF) microcapsules, using *in-situ* polymerization technique. In addition, Tung oil modified with corrosion inhibitor was also investigated. The synthesized spherical microcapsules were dispersed in zinc phosphate based epoxy primer coating. The microcapsule loading in the coating was optimized for self-healing ability as well as corrosion resistance and mechanical properties of the coating. The optimized coatings showed excellent healing effect along with superior corrosion resistance and mechanical properties.

Introduction

Self-healing coatings mimic natural healing process, similar to the healing of damaged skin [1]. Therefore self-healing coatings are very attractive as they can assure durability of the coated components even after damages in the coating due to chemical or mechanical reasons. Basic principle of self-healing coating is to heal the damaged area utilising a buffer stock of either the raw materials, or quick healing materials or an embedded corrosion inhibitor [2, 3]. The engineering aspect of self-healing is to store these core constituents in a suitable form as buffer within the microcapsules, incorporated in coating matrix.

Three main methods of achieving barrier restoration in self – healing coatings are; (i) intrinsic self-healing; (ii) capsule based self-healing and (iii) vascular self-healing [1]. In their previous work, authors already developed self-healing coatings, using the capsule based approach. Microcapsules loaded with linseed oil were synthesized in aqueous media using urea-formaldehyde (UF) as shell material [4]. The coatings impregnated with the optimized amounts of these microcapsules (i.e., 3 wt%) showed excellent self-healing effect [4]. Other studies have also reported self-healing coatings using linseed oil [5-7].

A similar approach was investigated in the present study, but with Tung oil as healing material. This work is novel as compared to other reported study on use of Tung oil as healing agent [8] in the sense, Tung oil was also modified with the addition of a corrosion inhibitor. In this work, improved performance of corrosion inhibitor in synergy with zinc phosphate pigments were achieved using epoxy zinc phosphate primer system as self-healing coatings.

Experimental

Materials

Microcapsule wall-forming materials, namely, urea, formaldehyde (37 wt% formaldehyde in water) solution, ammonium chloride, resorcinol, triethanolamine (TEA) and hydrochloric acid (HCl), were procured from Merck Co. (Mumbai, India). The core ingredients such as Tung oil containing 0.8 wt% cobalt napthenate and 1.9 wt% zirconium octoate driers, surface active agent Fynol P, and the zinc phosphate epoxy primer, were purchased from local sources. Corrosion inhibitor Halox 550WF was procured from Engichem Specialities Pvt. Ltd. (Mumbai, India). All the chemicals were used as it is, without any further purification.

Preparation of Microcapsules

The microcapsules containing Tung oil and corrosion inhibitor as core ingredients, and urea-formaldehyde as shell material, were prepared by in-situ polymerization technique following the modified synthesis process as described in our earlier publication [4].

The urea-formaldehyde (UF) pre-polymer was prepared by stirring 5 g of urea and 12.67 g of formaldehyde in a 100 mL beaker at 300 rpm until a clear solution was obtained. The pH of the solution mixture was adjusted at 8-9 using TEA, before it was heated to 70°C and held for 1 h, using an oil bath.

In a 250 mL three neck flask, 120 mL of deionized (DI) water along with 2 mL of surface active agent Fynol P was mixed for 15-20 min. Tung oil (25 mL) with and without corrosion inhibitor (Halox 550 WF) was slowly added as oil phase, with continuous stirring to form an emulsion. The emulsion was allowed to stabilize at 300 rpm for 30 min, followed by drop-wise addition of UF pre-polymer. After stirring for 30 min, 0.5 g resorcinol and 0.5 g ammonium chloride were added, followed by adjusting the pH of

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the emulsion to 2-3, using 5 wt% HCl. The reaction mixture was slowly heated to 55-60^{o}C in oil bath for 3 h, before allowing it to cool down to the room temperature, followed by filtration under reduced pressure. The microcapsules thus prepared were washed thoroughly with water and xylene to remove final traces of oil and any other foreign contamination. Free flowing microcapsules were obtained after vacuum drying at 50 ^{0}C for 48 h.

Characterization techniques

The mean diameter of microcapsules and shell wall thickness were determined using an optical microscope (Olympus GX5) that was equipped with image analyzing software (Olysia m3). The surface morphology of the synthesized microcapsules was investigated using scanning electron microscopy (SEM) (Hitachi S-3400N). The spectra of microcapsules containing tung oil with and without Halox 550WF were recorded on Fourier transform infrared spectrophotometer (Jasco FT/IR 6100). The percentage oil content in core was determined using solvent extraction method (Soxhlet process) as reported elsewhere [4-8].

Preparation of Self-Healing Coating

For preparation of self-healing coatings, microcapsule incorporation was performed by a two-step process as described elsewhere in detail [4]. In the first step, homogeneous dispersion of microcapsules was prepared in 10 mL of solvent mixture containing 30% xylene and 70% toluene. The dispersion process was assisted using water bath ultra sonicator for 30 min. The second step consisted of incorporation of dispersed microcapsules into zinc phosphate primer. A known quantity of microcapsule dispersion was added into the coating, followed by stirring for 30 min, using a three-blade mechanical disperser.

The self-healing coating thus prepared was applied on commercial grade mild steel substrates. The sizes of the substrates were 3 in. x 6 in. x 0.0197 in. The Mild steel substrates were rinsed with acetone to remove all the dirt and oil contaminations, followed by scrubbing them with 200 mesh size grit paper. A coating with a uniform thickness of 50-60 µm (as measured using Dry Film Thickness Gauge) was applied using a four-way applicator.

The coating was allowed to cure for 7 days in ambient air. For investigating the self-healing ability and corrosion resistance, the coating was artificially scribed with a sharp needle of 0.015 mm tip radius at a load of 500 g and was allowed to heal in ambient air condition. The compositions of the coating systems investigated in this study are listed in Table 1.

Table 1: Control and self-healing coating composition

Coating System	Microcapsules		Concentration of Microcapsules
	Core constituents	Shell Material	
A	-	-	0 wt%
B	Tung oil	UF	3 wt%
C	Tung oil + Halox 550WF	UF	3 wt%

Determination of Mechanical Properties

For possible use as commercial coating systems various mechanical tests were carried out; such as adhesion test (ASTM D3359-09 [9]), impact hardness (ASTM D2794-93[10]) and flexibility test (ASTM D522-13 [11]).

Results and Discussion

Microcapsule characteristics

Figure 1 shows optical micrograph of the microcapsules formed using UF as shell material, Tung oil and Tung oil modified with corrosion inhibitor (Halox 550WF). The formation of UF shell with Tung oil and Tung oil + Halox 550WF as core constituent is clearly visible from Figure 1. The shape of microcapsules is generally not spherical and they also vary in size and shape. The average size of microcapsules is in the range of 25-45 µm with shell wall thickness of around 2 µm. The shells were initially spherical as shown in Figure 2a. However, with increase in exposure time, the shell acquires various shapes (Figure 1). Morphology of the outer surface was rough, as shown in Figure 2b, which has been attributed to the deposition of UF nano-particles with high molecular weight [12]. The compact, uniform, hollow and smooth morphology of microcapsule inner shell provides excellent conditions for retaining core constituents without any premature leakage in the service life [12, 13]. Also, the rough outer structure provides excellent anchoring with the coating matrix, easing its breakage due to stress generated in the damaged region [4, 14].

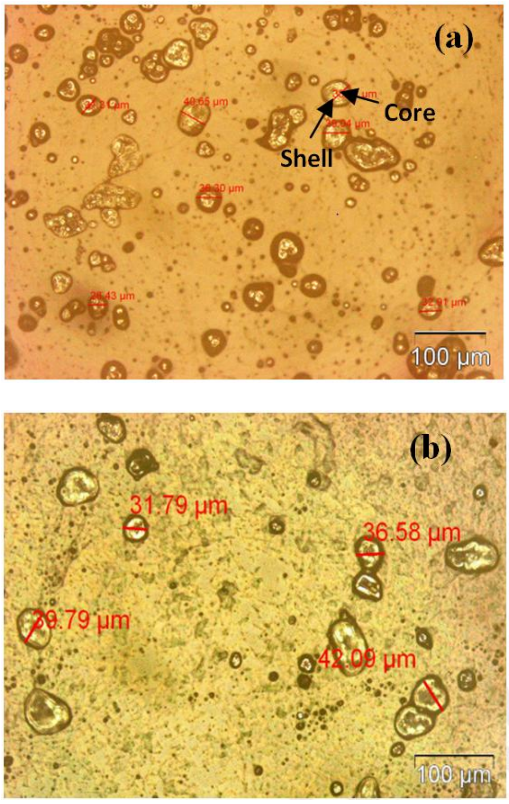

Figure 1: Optical microscopy images of microcapsules consisting of (a) Tung oil and (b) Tung oil + Halox 550WF

To confirm the presence of pristine Tung oil (TO) and UF in microcapsules (TOMC) and Tung oil + Halox 550WF and UF in microcapsules (TOMC + 550WF), FT-IR spectra of Tung oil, Tung oil along Halox 550WF and UF separated from microcapsules by Soxhlet process were recorded (Figure 3) following the reported procedure [4-7, 13-17]. In the case of UF sample, the spectrum had the characteristic peaks of 3286 cm^{-1} (N-H stretching), 3069 cm^{-1} (C-H stretching), 1655 cm^{-1} (C=O stretching), 1527 cm^{-1} (N-H bending), 1373 cm^{-1} (C-H bending) and 1183 cm^{-1} (C-N stretching). Characteristic peaks of 2930 cm^{-1} (O-H stretching), 2853 cm^{-1} (C-H stretching), 1748 cm^{-1} (C=O stretching), 1642 cm^{-1}

(C=C symmetric stretching) and 1463 cm^{-1} (C-H bending) were attributed to the Tung oil (TO) spectrum.

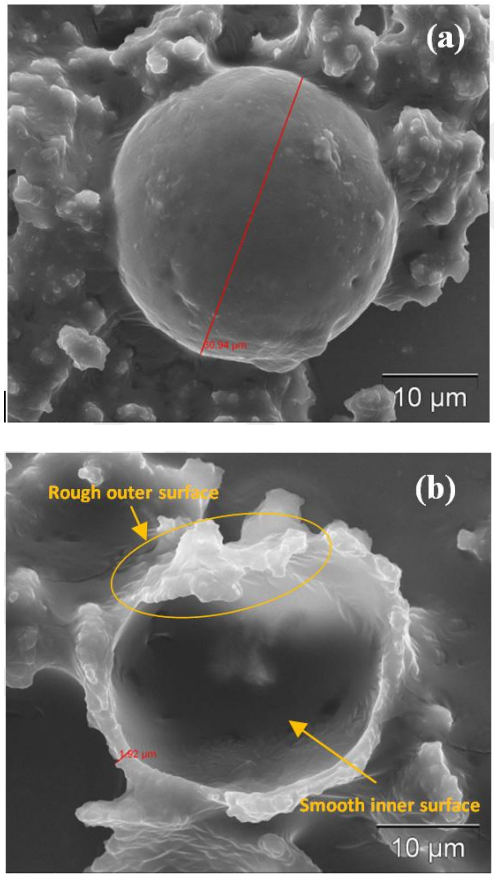

Figure 2: Scanning electron microscopy images of microcapsules (a) outer surface and (b) inner surface.

The spectrum of TOMC microcapsule contained all the characteristic peaks of both UF and Tung oil. Likewise, the spectrum of TOMC + 550WF microcapsules were characterized by all the characteristic peaks of UF along with 2935 cm^{-1} (O-H stretching), 2855 cm^{-1} (C-H stretching), 1652 cm^{-1} (C=C symmetric stretching), 1467 cm^{-1} (C-H bending) and 1744 cm^{-1} (C=O stretching) corresponding to TO + 550WF, confirming the presence of corrosion inhibitive additive in TOMC + 550WF microcapsules. Additionally FT-IR spectrum of 550WF has been included for the ready reference. Also, the characteristic peaks of each material along with their corresponding frequencies have been summarized in the Table 2 for easier reading.

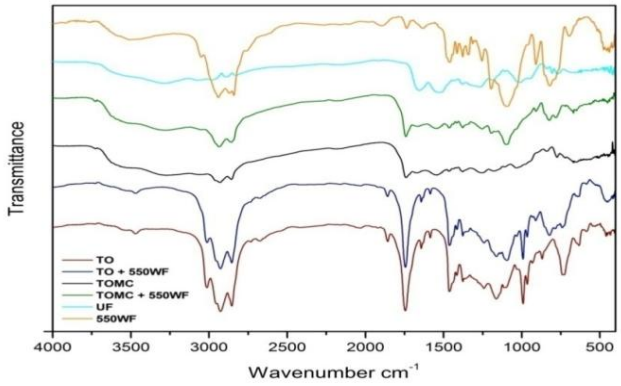

Figure 3: FT-IR spectra of microcapsules containing Tung oil with and without Halox 550WF, Tung oil, Halox 550WF and urea-formaldehyde polymer.

Table 2: FT-IR characteristic peaks

Material Details	Characteristic peak/ Bond					
TO	2930 cm^{-1} (O-H stretching)	2853 cm^{-1} (C-H stretching)	1748 cm^{-1} (C=O stretching)	1642 cm^{-1} (C=C symmetric stretching)	1463 cm^{-1} (C-H bending)	
TO + 550WF	2935 cm^{-1} (O-H stretching)	2855 cm^{-1} (C-H stretching)	1652 cm^{-1} (C=C symmetric stretching)	1467 cm^{-1} (C-H bending)	1744 cm^{-1} (C=O stretching)	
TOMC	2930 cm^{-1} (O-H stretching)	2853 cm^{-1} (C-H stretching)	1748 cm^{-1} (C=O stretching)	1642 cm^{-1} (C=C symmetric stretching)	1463 cm^{-1} (C-H bending)	
TOMC + 550WF	2935 cm^{-1} (O-H stretching)	2855 cm^{-1} (C-H stretching)	1652 cm^{-1} (C=C symmetric stretching)	1467 cm^{-1} (C-H bending)	1744 cm^{-1} (C=O	
UF	3286 cm^{-1} (N-H stretching)	3069 cm^{-1} (C-H stretching)	1655 cm^{-1} (C=O stretching)	1527 cm^{-1} (N-H bending)	1373 cm^{-1} (C-H bending)	1183 cm^{-1} (C-N stretching)

In view of above, it is evident that Tung oil, with and without Halox 550WF had been successfully encapsulated in the UF shell. The percentage oil content of prepared microcapsules was determined using Soxhlet process [4-8], for the extraction time of 5 h. The percentage oil content of microcapsules containing Tung oil and microcapsules containing Tung oil + Halox 550WF was evaluated to be 85 % and 82% respectively.

Evaluation of coating dispersed with Microcapsules

The healing ability of the coating systems "A", "B" and "C" (refer to Table 1) were examined using optical microscopy as shown in Figure 4 and Figure 5. The coating embedded with microcapsules containing Tung oil (Figure 5b) and tung oil + corrosion inhibitive additive (Figure 5c) healed seamlessly within 24 h of scribing. The self-healing action in the artificially scribed region is attributed to the release of Tung oil from the ruptured microcapsules, followed by drying in ambient air. A thin and uniform film of dried Tung oil formed, presumably by oxidative polymerization of unsaturated fatty acids present in the Tung oil, as evidenced in the literature [8]. In the absence of Tung oil, as in the case of the coating devoid of microcapsules (Coating A), no healing was observed (Figure 5a). SEM images (Figure 6) for supporting the findings of the corresponding optical observations for the healing or lack of it.

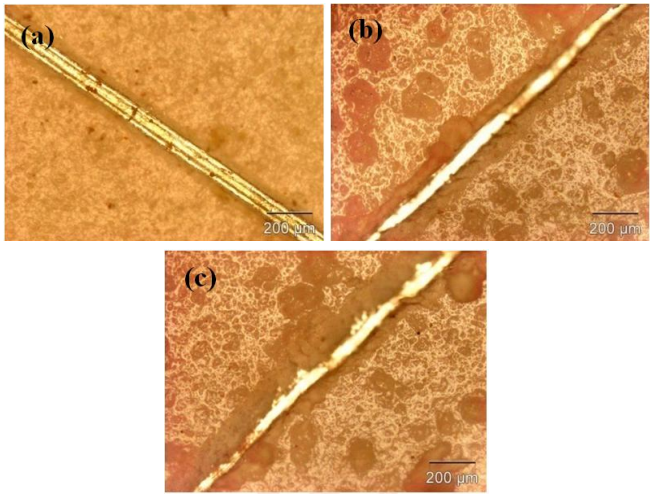

Figure 4: Optical microscopy images showing self-healing ability after 0 h of scribing with sharp needle for different coating systems (refer Table 1): (a) A, (b) B and (c) C in ambient air

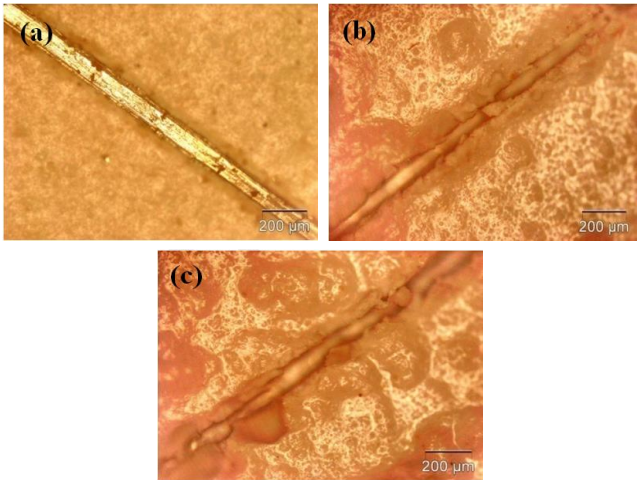

Figure 5: Optical microscopy images showing self-healing ability after 24 h of scribing with sharp needle for different coating systems (refer Table 1): (a) A, (b) B and (c) C in ambient air

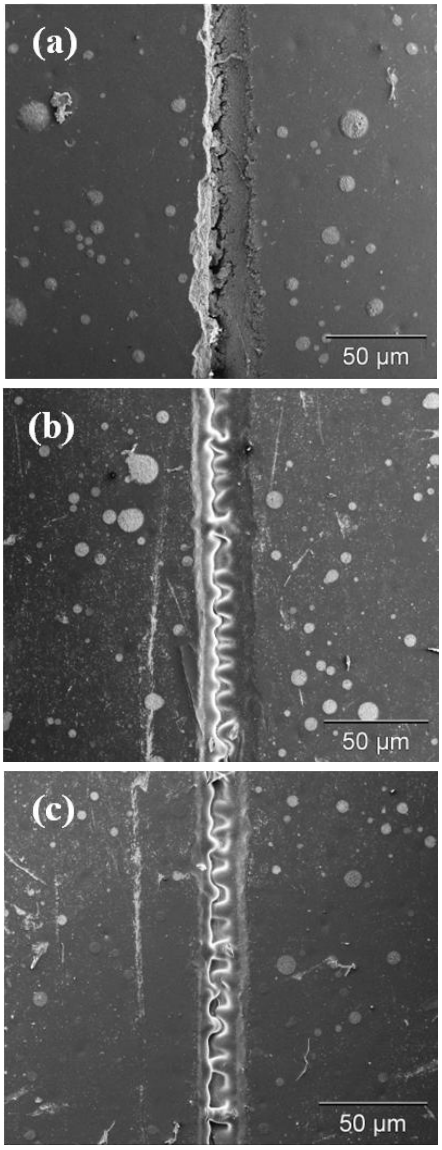

Figure 6: SEM images showing self-healing ability after 24 h of scribing with sharp needle for coating different systems (refer Table 1): (a) A, (b) B and (c) C in ambient air

Performance evaluation of modified coatings

Having established the ability of the modified coatings to heal the microscopic scratches, further analysis was carried out to study the effect of microcapsules on the physical and performance properties of the coating.

Corrosion resistance evaluation using immersion test

For examining the anti-corrosive performance of the self-healed areas, the coating systems A, B and C were immersed in 3.5% NaCl solution. The coating surface was artificially scribed through the cured film until the underlying metal was exposed [4-7]. The artificial scribe was made diagonally to form a cross-cut pattern as seen in Figures 7 and 8. The test was performed to accelerate the rate of corrosion, and visually observe the deterioration of scribed region and the surface of the coating. It was observed that the coating system "A" (that did not contain any Tung oil or inhibitor) started blister and flash rust was visible within 48 h of its exposure to the aqueous salt solution. Extensive rust formation and peeling of coating in the scribed region along with large number of blisters and rust on the surface was observed with increasing in the duration of exposure (Figures 7a and 8a).

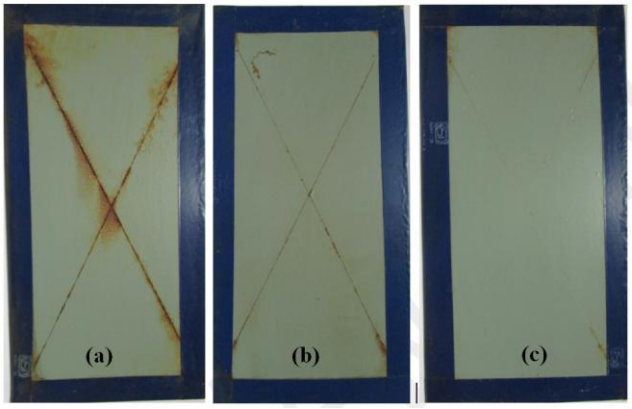

Figure 7: Coating surface after 300 h of immersion in 3.5% NaCl solution; (a) coating system A, (b) coating system B and (c) coating system C (refer Table 1).

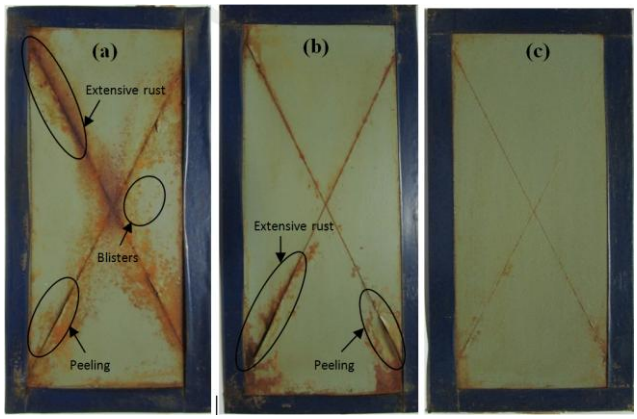

Figure 8: Coating surface after 600 h of immersion in 3.5% NaCl solution; (a) coating system A, (b) coating system B and (c) coating system C (refer Table 1).

However, coating system "B" (that contained Tung oil) showed only minor flash rust formation in the damaged areas till 300 h of exposure (Figure 7b). Accelerated corrosion activity was observed with increase in the time of exposure forming blisters, rust and slight peeling in the scribed region at the end of 600 h exposure, as shown in Figure 8b. Surface and scribed region of coating system

"C" (that contained both Tung oil and inhibitor) were free from blistering and rust formation until 300 h of exposure (Figure 8c), and only after exposure for 600h, slight rust was observed in the scribed area (Figure 8c).

The superior anticorrosive performance of coating system "C" was due to the healing action, provided by the excellent film forming capabilities of tung oil along with the improved inhibitive and adhesive functionality offered by the corrosion inhibitor (Halox 550WF). The improved resistance to corrosion offered by coating system "B" was again due to the healing capability offered by flow of tung oil in contrast to poor corrosion resistance of coating system "A", devoid of self-healing constituents.

Mechanical properties

The adhesion strength of coating systems A, B and C were determined as per ASTM D3359-09 [9] and it was found that 0% of grid area was detached, confirming an adhesion rating of 5B for each of the three coatings. The flexibility test, conducted as per ASTM D522-13 [11] suggested no cracking or chipping of areas subjected to elongation at mandrel diameter 3mm in the case of any of the three coatings. The impact test (ASTM D2794-93[10]) indicated (Figure 9) no significant differences in the mean impact strengths of the three coatings. No cracking, chipping or delamination of coated film was observed, as examined by pin-hole detector and magnifier. For reproducibility of results, all the tests were performed on multiple test panels. The investigations showed no deviation in the adhesion, flexibility and impact ratings of coatings, embedded with microcapsule (coating systems B and C) when compared with the control coating (A). Thus, it can be seen that no loss of adhesion, flexibility and impact properties were observed due to incorporation of microcapsules.

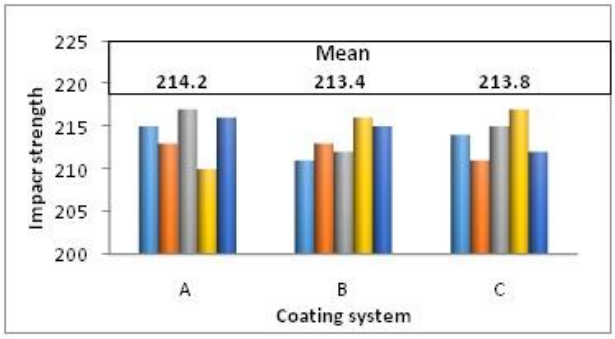

Figure 9: Impact strength of coating systems A, B and C (refer Table 1).

Summary

The main objective of the present work was to formulate self-healing coatings using Tung oil as a healing agent by capsule based approach to achieve maximum self-healing effect at optimized concentration of microcapsules. The scheme of formulation, optimized concentration of Tung oil and the synthesis of microcapsules was taken from experience of the authors' earlier work on linseed oil [4].

As compared to the reported work on linseed oil/Tung oil, where 50-60 ml of healing material has been used, a much lower concentration, i.e., 25 ml was used for synthesis of microcapsules in the present work [8, 13, 14]. Another important finding concerns the size and dimension of microcapsules. It was found that the microcapsules of 25-45 µm size and a concentration of 3 wt% in the coating formulation, resulted in faster self-healing performance as compared to 50-350 µm size microcapsules and 10-15wt% microcapsule concentration in coating formulations reported earlier [5, 8, 13, 14, 17]. The reduced sizes of microcapsules allowed reduction in coating thickness by 50%, i.e. 50-60 µm in the present study as compared to 100-250 µm as reported by Jadhav et al. [6], Samadzadeh et al. [8], Hatami Boura et al. [5] and Nesterova et al. [17]. It is noted that, optimized microcapsule sizes of 25-45 µm allows effective dispersion and better distribution of microcapsules in the coating matrix, increasing the probability of microcapsules to be present at the damage site.

Superior resistance to corrosion upto 600 h of immersion in NaCl solution was witnessed by modifying encapsulated Tung oil with corrosion inhibitive additive; Halox 550WF. The coating showed improved resistance to blistering and peeling without any sacrifice of adhesion and mechanical properties at thinner coating thickness when compared to Jadhav et. al., where extensive rust was observed at 480 h of exposure in the scribed region of the coating surface, embedded with microcapsules containing titanium based corrosion inhibitor [6].

The study of anti-corrosive mechanism of self-healing coatings and the detailed investigation of role of inhibitor and its effect on corrosion resistance behaviour is being undertaken as an extension of present work and will be published separately.

Conclusions

Tung oil along with driers and Halox 550WF were successfully encapsulated in UF shell using *in-situ* polymerization technique. Infrared spectroscopy confirmed the presence of tung oil and inhibitor as the core constituents. The prepared microcapsules showed compact smooth inner and rough outer surface, providing hollow structure, retaining core constituents without leakage and better anchoring with the coating matrix. Self-healing coating systems "B" and "C" showed excellent healing capabilities within 24 h of inducing artificial damage. Immersion test results indicate improved anti-corrosive performance of coating system "B" and "C" compared to coating system "A". The superior anticorrosive functionality of coating system "C" was due to the presence of corrosion inhibitor additive, providing inhibitive and adhesion promoting capabilities. Adhesion, impact and flexibility test results confirm no sacrifice in the performance of self-healing coatings embedded with microcapsules.

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