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Urea-phenol-formaldehyde microcapsules containing linseed oil for self-healing anticorrosive coating applications

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ABSTRACT

Novel self-repairing Urea-Phenol-Formaldehyde (UPF) microcapsules containing linseed oil were prepared via in-situ polymerization in an oil-in-water emulsion. The main purpose of encapsulation is to control the release of linseed oil, when external conditions such as mechanical stress or energy cause microcapsules to break. These controlled release mechanisms of linseed oil make them suitable for application in self-healing coatings. Chemical structure analyses of microcapsules were studied by Fourier transform infrared spectroscopy (FTIR), optical microscopy and scanning electron microscopy for their structural & morphological illustrations. Controllable particle sizes were determined under optical microscope and as well using particle size analyzer. To determine the healing efficiency, the microcapsules, were incorporated in the epoxy coatings in varying proportions. The effects of the same on anti-corrosion performance was carried out in 5% NaCl aqueous solution (ASTM B117) and Decreasing trend of pencil hardness, scratch hardness, Impact resistance with the increase in concentration of microcapsules was observed. Chemical resistance could also be attributed to the presence of aromatic structures in epoxy which impart chemical stability. Secondary hydroxyl moiety in epoxy chain forms hydrogen bonding with the metal substrate that would contribute to good adhesive forces. Epoxy coatings incorporated with microcapsules showed better corrosion resistance than neat epoxy coating, where neat epoxy coating showed rust and spreading of rust observed on tested panel. Mechanical properties decreased on incorporating microcapsules into epoxy matrix, hence development of mechanical properties without effecting the corrosion properties shall be studied further. Copyright © 2016 VBRI Press.

Keywords: Anticorrosion, microencapsulation, self-healing, linseed oil, urea-phenol-formaldehyde.

Introduction

Corrosion of metal causes enormous financial losses which additionally reduce our natural's resources and so, it is a critical issue for all, over world [**1**]. To protect the metal from corrosion, approach towards great variety of organic protective coatings is made. These protective coatings included corrosion inhibitors on metal substrates, which are restricted or steadily reduced in many countries due to their environmental toxicity [**2**, **3**, **18**]. These organic protective coatings during service life, are always inevitably subjected to unexpected damages and micro cracks through which corrosion occurs gradually. Such defects are hard to identify and at last metal may lose its functional properties [**4**, **5**] .Usually, this problem is solved by inspection and replacing the damaged parts. However, it's time consuming and expensive method since the only option available is to replace the damaged part [**6**]. Therefore, it becomes crucial to build up some techniques by means of which this crack formation can be avoided or even if crack is formed, it should be healed automatically. So, the most suitable option is to heal the crack for which scientists have taken motivation from biological systems which have inbuilt ability to repair damage via healing mechanisms.

In last decade, scientists and researchers are on track for developing such systems called as "Self-healing". There has been growing interest in use of self-healing polymer for corrosion protection via healing of micro cracks [**18**, **19**,**16**]. Till date, self-healing techniques has been demonstrated by three conceptual approaches namely capsule-based healing systems, vascular healing systems, and intrinsic healing polymers [**8**, **9**]. Intrinsic materials are those which possess latent self-healing ability inherently when triggered by damage or external stimulus. This can be accomplished by thermally reversible reactions, hydrogen bonding, ionomeric coupling, dispersed melt able thermoplastic phase or molecular diffusion. Vascular self-healing materials sequester the healing agent in a network in the form of capillaries or hollow channels, which are interconnected one-dimensionally (1D), two-dimensionally

(2D), or three-dimensionally (3D). Capsule based systems needs to encapsulate healing agents in polymeric shell by various polymerization techniques, although not all of them are autonomous and need some external stimulus such as elevated temperature.

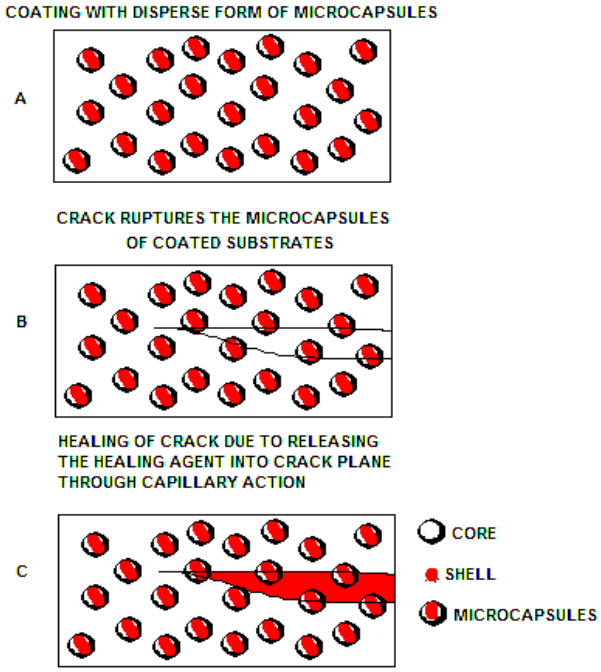


Fig. 1. Self-healing concept (a) Coating with disperse form of microcapsules; (b) Crack ruptures the microcapsules of coated substrate (c) healing of crack due to releasing the healing agent into the crack plane through capillary action.

Microencapsulation technique for self-healing applications (**Fig. 1**) has been successfully initiated by White *et al.* [**5**] via dicyclopentadiene (DCPD) encapsulation in urea-formaldehyde polymeric shell. DCPD microcapsules and grubb catalyst are dispersed in the epoxy matrix uniformly. Whenever; crack is generated on surface, dispersed microcapsules ruptures and healing agent releases into the crack plane through capillary action [**10**, **11**]. Encapsulation of self-healing agent in shell wall is an attractive way of storing as well as shielding, these from environment till required for fulfilling appropriate applications. In two components self-healing system micro crack healing occurs probably only when, the both ingredients are present in one place at same time and this is huge draw-back of system. Hence, smart approaches to prepare catalyst free self-healing coatings system is carried out. In this sense, the encapsulation of a vegetable drying oil and liquid diisocyanates creates a one-part self-healing corrosion resistant coatings [**12-16**]. But, liquid diisocyanate monomer is toxic in nature and hence use of isocyanates is limited for one-part self-healing system. Sol–gel coatings prepared from glycidoxypropyltrimethoxysilane, tetraethoxysilane and methyltriethoxysilane with 2 wt.% of sodium montmorillonite were studied for corrosion protection, wherein pH has a direct impact on the nanoclay dispersion as specific interactions between the silanol groups and the nanoclays were observed from FT-IR and indirectly confirmed by the study of the influence of the delay between pH adjustment and addition of the precursors on the properties of the coating, interactions were correlated to the corrosion protection efficiency [**21**]. The mild steel surface has been modified to impart anticorrosion and antibacterial properties through a dip coating method followed by thermal curing of a mixture containing amine terminated cyclotriphosphazene and functionalized titanium dioxide nanoparticles reinforced benzoxazine based cyanate ester composite, nanocomposites coated mild steels have displayed a good chemical stability over long immersion in a corrosive environment [**22**]. Functionalized fullerene C60 (FC60) and functionalized graphene (FG), were incorporated into the epoxy matrix for tribological and anti-corrosion performances of epoxy coatings, tribological and anti-corrosion results indicated that composite coatings showed a lower friction coefficient, wear traces area and higher anti-corrosion in comparison with neat epoxy, owing to the balance of reinforcement, lubrication and barrier properties of nanofillers and cracks generated by them, and optimal additive concentration of FC60 and FG both were 0.5 wt.%. FC60/EP coatings exhibited better tribological performance but worse corrosion resistance ability compared with FG/EP coatings due to the different shapes of nanofillers [**23**]. Paint formulation was made by blending the as-synthesized nano ZnO with a natural organic resin; cashew nut shell liquid (CNSL) and surface coatings were developed over glass and metal substrates. ZnO–CNSL paint coatings were further studied for NIR reflectance, optical transparency and hydrophobic surface property. Its effective corrosion resistance has been validated with highly corrosive Mg-alloy substrates [**24**]. Microcapsules shell wall should have enough mechanical strength to survive under shear stress which is generated during incorporation and application of coatings.

The selection of a suitable shell material that withstands under high shear stress is important. A number of polymers have been used as shell materials and these include urea–melamine–formaldehyde, urea–formaldehyde, melamine–formaldehyde, gelatine–formaldehyde, toluene-2, 4-diisocyanate and diethylene triamine and polyurethane. In our work, we introduce urea-phenol-formaldehyde (UPF) as shell materials for linseed oil microcapsules synthesis via in situ polymerization. Phenol has cyclic structure with three active functional sites as consequently shell material form three diamensional structures. UPF shell materials give better hardness than urea-formaldehyde (UF) polymeric shell materials. Simultaneously, the heat resistance, acid resistance and alkali resistance is also improved. UPF microcapsules are synthesized and thereafter incorporated into epoxy base coatings in various proportions via ultrasonic techniques. Healing efficiency of the microcapsules coatings is studied by salt spray test.

Experimental

Materials

Phenol, urea, resorcinol and formaldehyde used as shell materials were purchase from S D Fine-Chem Ltd Mumbai, India. Linseed oil used as core material purchase from (Calf Brand, Pune, India). Poly vinyl alcohol (PVA) used for

stabilizing the core and Ammonium Chlorides were procured from S D Fine-Chem Ltd Mumbai, India. Ammonia solution and Hydrochloric acid was used to control the pH of reaction mixture. All commercial chemicals were used without further purification in this study.

Fig. 2. Synthesized microcapsules.

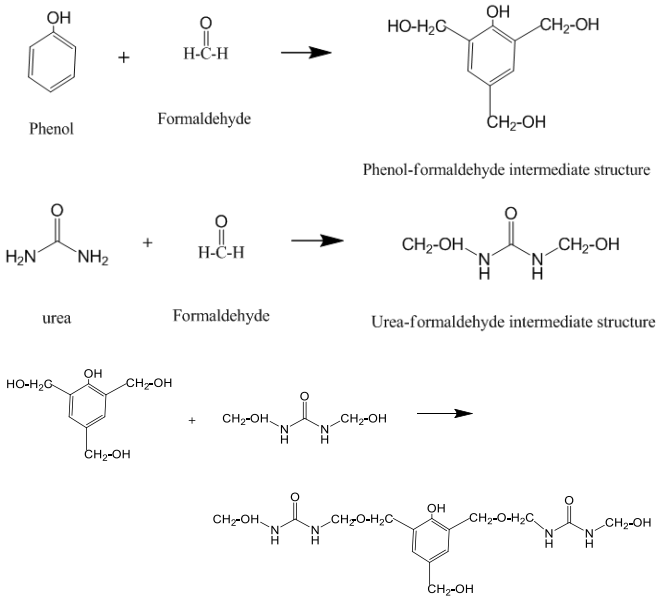
Methods

Novel self-repairing UPF surrounded microcapsules containing linseed oil were prepared by in situ polymerization in an oil-in-water emulsion. At room temperature, 5 wt % aqueous solution of polyvinyl alcohol was mixed with distilled water and linseed oil containing 0.5 wt % cobalt octoate drier in a 250 ml beaker. Stabilization of oil was carried out in probe sonicator for 15 min and then transferred into 250 ml four-necked flask. Phenol and ammonium chloride were dissolved in above mixture at 500 rpm agitation. Thereafter pH of mixture was adjusted to approximately 7 by using ammonia solution and allowed to stir continuous for 30 min. Formaldehyde was added drop wise and temperature was raised gradually to 65°C and maintained for 2 h. After that pH was again adjusted with reference to 3 by using 5 wt % of HCl solution. After achieving desired pH, stoichiometric amount of resorcinol and urea was added to the reaction mixture and stirred for about 3 hrs. After completion of reaction, mixture was cooled to ambient temperature and microcapsules from the suspension were recovered by filtration under vacuum. These microcapsules were rinsed with water, washed with xylene to remove suspended oil and monomer. The obtained capsules were dried under vacuum to obtain UPF microcapsules **(Fig. 2)**.

The above prepared UPF microcapsules were incorporated in epoxy coating. The microcapsule/epoxy coatings were prepared via microcapsules in varying proportion in epoxy coatings by ultra sonicator for 30 minutes. Then microcapsules/epoxy coatings were reacted with polyamide hardener in stoichiometric amount to cure coating.

Characterization

Chemical structure of the microcapsules was identified by Fourier Transform Infrared spectrophotometer (NICOLET 5700 Thermo Electron Corporation). The UPF microcapsules were visualized using an optical microscope and the surface morphology of microcapsules was observed via scanning electron microscopy, (LEO1455). The particle size was analyzed with a laser particle size analyzer (Microtrac X 100, Microtrac, Largo, FL, USA). Mechanical properties like pencil hardness, flexibility, scratch hardness, cross cut hardness as well as impact and Chemical properties of the epoxy coatings dispersed microcapsules were determined. Core content in microcapsules and Corrosion resistance of coatings were investigated.



Scheme 1. Shell formation process

Core content in microcapsules

Core content in microcapsules was calculated by extraction method in a soxhlet apparatus. Microcapsules were weighed (Mc) on sensible weight balance then crushed using pestle and mortar and transferred to a thimble of known weight. Extraction was carried out using xylene as a solvent for 2 hrs. Then the suspension was filtered through filter paper to separate shell material. Each measurement was carried out in duplicate. The collected shell material dried in oven and final weight (Ms) was taken. Microcapsules oil content was calculated as given below:

$$Oil\ content\ (\%) = \frac{(Mc - Ms)}{Mc}$$

where, Mc and Ms are the microcapsules and shell mass of microcapsules, respectively.

Corrosion resistance of coatings

In this study, synthesis microcapsule incorporated in epoxy base paint and mixed with polyamide hardener in stoichiometric amount for curing. The epoxy coatings were applied on MS panel. After 7 days, of curing a cross-cut was induced by razor blade in neat epoxy coating and microcapsules incorporated epoxy base coatings. Corrosion protection properties of the coated panel were evaluated by

exposing the substrates to a salt spray as per ASTM B117 specifications.

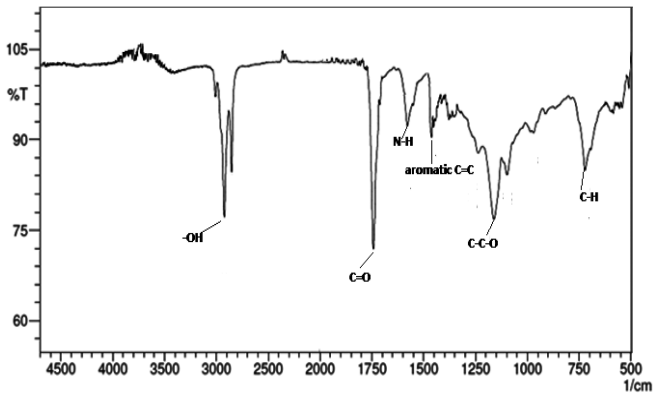


Fig. 3. FTIR of UPF microcapsules.

Results and discussion

Fourier transform infrared spectrophotometer analysis

FTIR spectra of UPF shell **(Fig. 3)**, shows transmissions band at 1462 cm^{-1} attributed to the C=C aromatic ring vibrations. Characteristic peak of N-H stretching vibration is observed at 1571 cm^{-1}. C-N stretching vibrations are visible at 1286 and 1142 cm^{-1}. The transmissions peaks are observed at 1454 cm^{-1} are attributed to the C=C aromatic ring vibrations, the peaks at 1161 and 1097 cm^{-1} are characterized peak of C=C=O asymmetric stretch, and C-H in plane deformations, respectively. The peak at 721 cm^{-1} imprints the C-H out of plane vibrations, also the peak 2862 and 2964 cm^{-1} denotes the C-H stretching vibration. However, for linseed oil, the main stretching absorptions were observed for C=O stretching vibrations at 1741 cm^{-1}.

Table 1. Mechanical Properties of neat and PF microcapsules epoxy coatings.

	Pencil Hardness (H)	Flexibility (mm)	Scratch Hardness (g)	Cross cut adhesion (B)	Impact (lb.cm)
Neat Epoxy Coating	5	0	2700	5	120
10% Microcapsules Epoxy coatings	5	0	2700	5	120
20% Microcapsules Epoxy coatings	5	0	2600	5	120
30% Microcapsules Epoxy coatings	4	1	2400	5	114
40% Microcapsules Epoxy coatings	4	2	2300	5	108

Surface morphology (SEM/OM)

The surface morphology **(Fig 4a, 4b)** of prepared microcapsules was studied using scanning electron microscope at X50 and X300 magnification. **Fig. 4a, 4b** illustrates the SEM image of UPF microcapsules at 600 RPM stirring rate. In the formation of UPF microcapsules, resorcinol plays an important role to combine; phenol formaldehyde and urea formaldehyde oligomers, leading to the formation of strong protective uniform shell over the active core material. Microcapsules find in uniform and circular shape with rough surface which gives good interfacial adhesion with coating matrix. The shape of microcapsules was found to be spherical when observed under optical microscope as well as in scanning electron microscope.

Mechanical properties

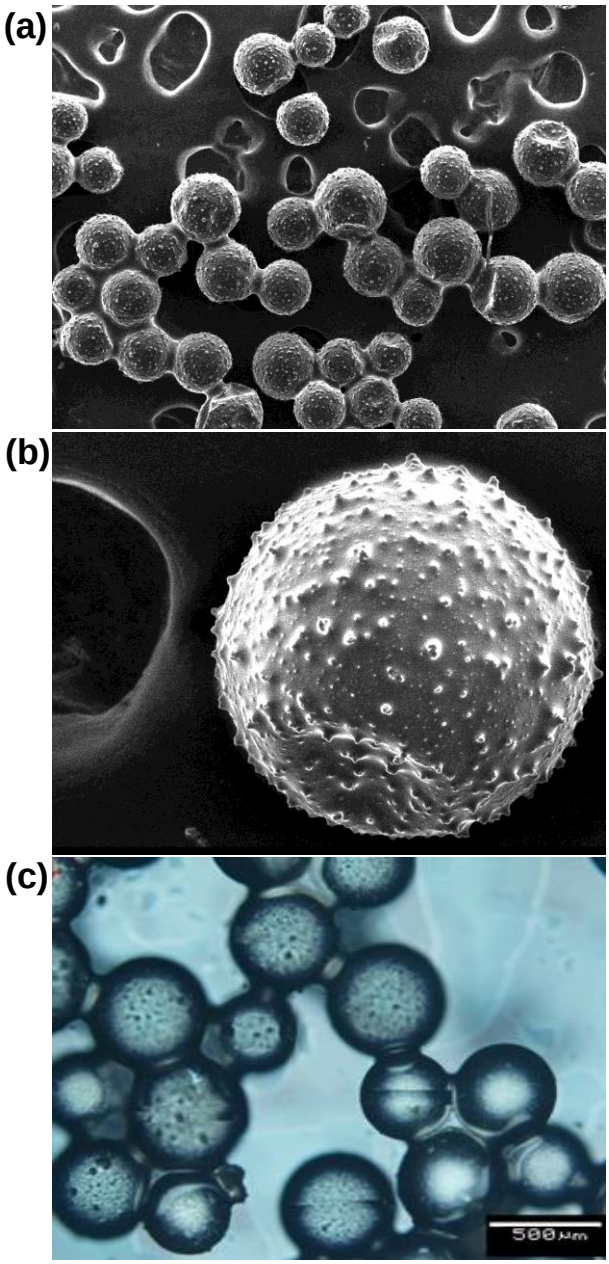


Fig. 4. Scanning electron microscope micrographs (a)X50, (b) X300 and Optical Microscope (c) UPF microcapsules.

The microcapsules incorporated epoxy coatings and neat epoxy coatings were evaluated for mechanical properties such as pencil hardness (ASTM D3363–00), scratch hardness, flexibility (ASTM D522–93a), cross-cut adhesion (ASTM D 3359 – 02), impact resistance (ASTM D 2794 – 93) see **Table 1**.

(a) *Adhesion*

The adhesion of coatings to metal substrate was measured using cross-cut method. It was observed that all the coatings exhibited good adhesion to metal substrate. The polar nature of secondary hydroxyl moiety in epoxy chain forms hydrogen bonding with the metal substrate that would contribute to good adhesive forces.

(b) *Pencil hardness*

Hardness of coatings was measured using pencil hardness. There has been a decreasing trend of pencil hardness with the increase in concentration of microcapsules. Hardness of the coating depends upon the cross linking density. The neat epoxy coating gives better hardness which may be due to the presence of high cross linked structure in the film makes them tough and also difficult to notch off. As microcapsule incorporation percentage increases, coating hardness decreases due to poor adhesion between capsules and epoxy coatings.

(c) *Scratch hardness*

Coatings were also evaluated for scratch hardness. Gradual decrease in scratch hardness was observed with increase in concentration of microcapsules. The epoxy coating gives better hardness which may be due to the presence of three dimensional cross linked structures in the film which makes them hard and also not easy to notch off. As microcapsule incorporation percentage increases, coating hardness decreases due to poor adhesion between capsules and epoxy coatings. The hardness could also be attributed due to the aromatic structures of monomer which impart chemical stability.

(d) *Impact resistance*

Capacity of coating to distribute load was calculated using falling ball impact test. As incorporation percentage of microcapsules increases in epoxy coatings were shown poor impact resistance as compared to the neat epoxy coating. Microcapsules incorporation was shown negative impact due to the non-homogenous distribution of capsules in coating matrix.

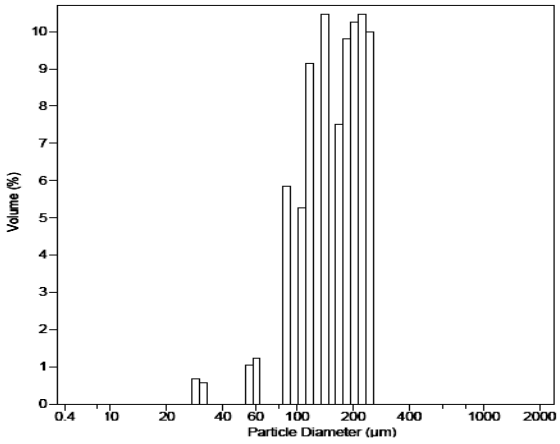


Fig. 5. Particle size histogram of PF microcapsules.

Chemical properties

All the coating systems were evaluated for their acid and alkali resistance by immersion method. Acid and Alkali resistance of coatings based on neat epoxy and microcapsules incorporated epoxy were investigated according to ASTM D 1308, see **Table 2**. The coatings showed excellent resistance to acid (5% HCl) and alkali (5% NaOH) without any defects such as blistering or loss of adhesion for 24 hours. This could be attributed to the cross-linked chemical backbone of the films suggesting complete curing of the coating systems. The excellent chemical resistance could also be attributed to the presence of aromatic structures in epoxy which impart chemical stability.

Table 2. Chemical Properties of neat and microcapsules epoxy coatings.

Sample	5 % NaOH sol^{n}	5 % HCl sol^{n}
Neat Epoxy Coating	Pass	Pass
10% Microcapsules Epoxy coatings	Pass	Pass
20% Microcapsules Epoxy coatings	Pass	Pass
30% Microcapsules Epoxy coatings	Pass	Pass
40% Microcapsules Epoxy coatings	Pass	Pass

Particle size analysis

Fig. 5 shows the particle size distribution of the prepared PF microcapsules containing linseed oil. The microcapsules' size ranges from 180 to 220 micron. It is observed that the microcapsules' size can be controlled by controlling the rate of agitation.

Salt spray test for studies anti-corrosion behaviour of coating

The concept of corrosion protection through autonomous healing system via atmospheric oxidation of oil has been demonstrated in this section. For this purpose, oil encapsulated using in situ polymerization techniques and introduced into an epoxy coating in varying proportions. Thereafter surfaces of mild steel panel are coated with neat epoxy coating and microcapsules incorporated epoxy coatings. After 7 days of coatings application, crosscut was made by razor blade up to the metal surface. Through the crack moisture and oxygen are transported to the metal-coating interface, and then these corrosive species start corrosion reaction, to deteriorate the properties of exposed mild steel surface.

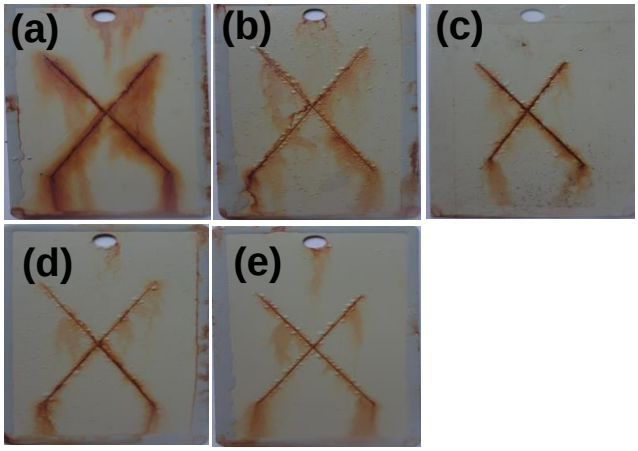


Fig. 6. Salt spray test performance of (a) neat epoxy coating (b) 1% microcapsules epoxy coating (c) 2% microcapsules epoxy coating (d) 3% microcapsules epoxy coating and (e) with 4% microcapsules epoxy coating.

The microcapsules incorporated coating, should break open capsules immediately to release healing material when

micro cracks are generated in the coating film. Healing of micro crack via core agent releases into the crack plane through capillary action provides an effective method to prevent corrosion. In above study, it was found that microcapsules epoxy coatings showed better corrosion resistance than neat epoxy coating. Microcapsules coatings were free from rust, blister and also there was no more spreading of rust along the tested panel. Better 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 **(Fig 6b – 6e)**. On the other hand, neat epoxy coating showed rust and spreading of rust observed on tested panel **(Fig 6a)**.

Conclusion

In this work, linseed oil along with drier was successfully microencapsulated in urea phenol formaldehyde microcapsules prepared by in situ polymerization techniques. Optical and Scanning Electron Microscopy confirmed that oil was successfully contained in the urea-phenol-formaldehyde microcapsules. The particle size distribution of these microcapsules was successfully controlled by the stirring rate. The material inside the UPF microcapsules used as a healing material remains intact on coating till it is required for crack filling application (self-healing application). The microcapsules filled coating imparted corrosion resistance properties via healing of cracks efficiently by oxidation. Mechanical properties decreased on incorporating microcapsules into epoxy matrix; hence improvement of mechanical properties without affecting the corrosion properties shall be studied further.

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