



Assessment of Anticorrosive Coatings with Multicore Microcapsules and Polyaniline Nanoparticles: A Novel Synergistic Approach

U. B. Gawai¹, P. S. Shisode², C. B. Patil*³

Abstract

The present investigation reports, successful preparation of polyaniline (PANI) nanoparticles and its improved corrosion resistance with addition of multicore microcapsules. The multicore microcapsules were synthesized by in-situ polymerization method, with oil in water emulsion technique separately and blends of Tung oil and Dehydrated Castor oil (20 % and 30 % DCO) were entrapped in urea formaldehyde (UF) micro containers. The surface morphology of prepared microcapsules was analysed initially by digital optical microscope and then with Scanning Electron Microscopy (SEM). The particle size of synthesized microcapsules was determined by particle size analyser. The core content of the microcapsules was determined by extraction process using Soxhlet apparatus. The synthesized microcapsules were then incorporated into epoxy coating to verify their self-healing properties. The improved corrosion resistance of PANI nanoparticles was then checked by incorporating them along with the synthesized microcapsules combinations into epoxy coating matrix. Corrosion protection of coated panels were analysed by immersion in 3.5 % NaCl and 0.5 M HCl solution and studied in comparison with pristine epoxy coated panels.

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KeyWords: Microencapsulation, Tung Oil and Dehydrated Castor Oil blend, Polyaniline nanoparticles, Anticorrosive coatings.

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Introduction

Metallic structures are continuously facing deterioration followed by steady degradation which in turn affects their performance during service life. It leads to premature failure in various technical fields such as aeronautics, electricity production plants, offshore oil and gas industry etc. It causes tremendous economic losses and thus, slows down of global economic growth [1]. It also exposes risk to human health as in metallic medical implant, industrial gas pipeline leakages, rusting of drinking water pipelines and failure of bridges etc. Therefore, it is important to choose the effective and affordable mode to decrease the deteriorating effect of corroding structures. The most common and cost-effective method is organic coatings, which increase the corrosion resistance and results long life durability of steel material [2]. However, these coatings suffer from mechanical or chemical action in their service life. Mostly, micro crack generated and propagated further to form, crack and thus exposes the underneath metallic substrate to corroding aggressive species. These micro cracks are difficult to detect and nearly impossible to repair by conventional methods [3-4], to overcome this issue self-healing materials were introduced by White and co-worker in 2001 [5].

Amongst various self-healing approaches, microencapsulation approach is the most efficient way to protect metallic structures from corrosive environment, as the micro crack generated in coating matrix, it breaks down the embedded microcapsules as a result it releases healing agent at damage part. Then released healing agents polymerizes on auto oxidation to repair the damage [6-15]. Nowadays, various self-healing mechanisms have been developed [16].

In microencapsulation approach the poly urea-formaldehyde shell material is extensively used along with various healing agents for epoxy resins like dicyclopentadine [17], amine and epoxy [18-19], Mercaptans [20], a variety of drying oils such as linseed oil [21], Tung oil and alkyd resins [22], Soyabean oil [23].

Drying oils are triglyceride of long chain unsaturated fatty acids used as auto-oxidative

healing agent in microencapsulation [24]. It was already reported that synthesis of microcapsules using phenol-formaldehyde shell material by in-situ polymerization method based on linseed oil as healing material having film forming ability due to aerial oxidation [25]. The capability of encapsulated Tung oil as a scratch healing agent for self-healing coatings, using urea formaldehyde as a shell material [26] and encapsulated linseed oil and Tung oil in a urea formaldehyde shell has been explained earlier [27]. The incorporation of PANI nanoparticles into the epoxy coating was studied which shows improved anticorrosion performance of PANI/epoxy coating matrix [28].

In continuation with these reported findings, we intended to prepare PANI nanoparticles /vegetable oil microcapsules/epoxy self-healing anticorrosive coatings. For these various combinations of microcapsules of blended dehydrated Castor oil and Tung oil were prepared and then characterized and incorporated along with Polyaniline nanoparticles in epoxy coating matrix. The anticorrosive performance of formulated epoxy coating was investigated synergistically by immersion study in 3.5 % NaCl and 0.5M HCl solution.

Experimental Section

Material:

The material used in experiment - Aniline (distilled). Ammonium persulphate, Hydrochloric acid, Methanol, Ammonium hydroxide, Urea, Formaldehyde, Resorcinol, Xylene, Ammonia solution, Ammonium chloride, and poly (Vinyl Alcohol) were purchased s d Fine Chemicals Ltd., Mumbai, India and used as such without further purification. Tung Oil, Dehydrated Castor oil and the primer were supplied by local supplier. Epoxy resin supplied by Shri Surya Coatings, Industries, Nashik, India used in an experiment was without further modification.

Synthesis of Polyaniline Nanoparticles:

Polyaniline nanoparticles were synthesized with simple chemical deposition technique as per literature reported method [29].

Synthesis of UF microcapsule:



Microcapsules of Tung oil and Dehydrated Castor oil blends (DCOT) were synthesized separately by the process of in situ polymerization using oil-in-water emulsion technique. The detailed description of the experimental procedure was followed from our previous literature reported findings [23]. The various combinations of drying oil for synthesis of microcapsules are given in Table 1.

Table 1. Combinations of drying oil for synthesis of microcapsules.

Prepared Drying Oil Combination	Tung Oil	Dehydrated Castor Oil
20 % DCOT	20.0 mL	5.0 mL
30 % DCOT	17.5 mL	7.5 mL

Characterization

The synthesized 20 % DCOT and 30 % DCOT microcapsules were analysed initially using optical microscope then subjected for morphological verification by scanning electron microscope (Nova Nano SEM 450). The particle size analysis was accrued out by particle size analyser. The quantity of oil content in UF microcapsule was extracted using Soxhlet apparatus; the extracted core and shell material were used for FTIR analysis (FTIR Shimadzu-8400). The self-healing efficiency was determined by incorporating the synthesized microcapsule into epoxy coating matrix. The physicochemical properties like gloss were determined for PANI/synthesized microcapsule/ epoxy coating. The detailed description of these characterizations was discussed in our previous publication [23].

Result and Discussion:

Surface morphology

The synthesized 20 % DCOT and 30 % DCOT microcapsules were primarily analysed by Olympus optical microscope as shown in Figure 1 and 2 (a, b) which revealed successful synthesis of spherical microcapsules. Then morphology of prepared microcapsules was verified field emission scanning electron microscopy. The FESEM images in Figure 3 and 4 (a, b) shows that microcapsules are spherical in shape having a rough and non-porous shell wall. Rough surface of the shell wall gives good adhesion with coating

matrix [31]. The synthesized PANI nanoparticles were initially verified with the help of SEM (Figure 5) and then subjected to FTIR study.

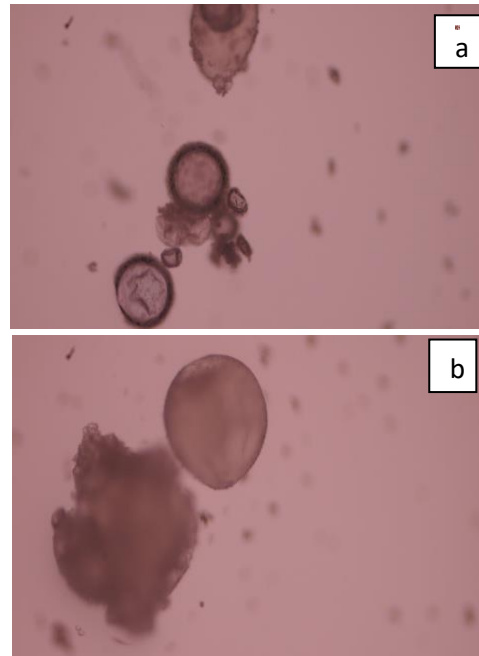


Figure 1. Optical images of synthesized (20 % DCOT) oil microcapsule (a, b).

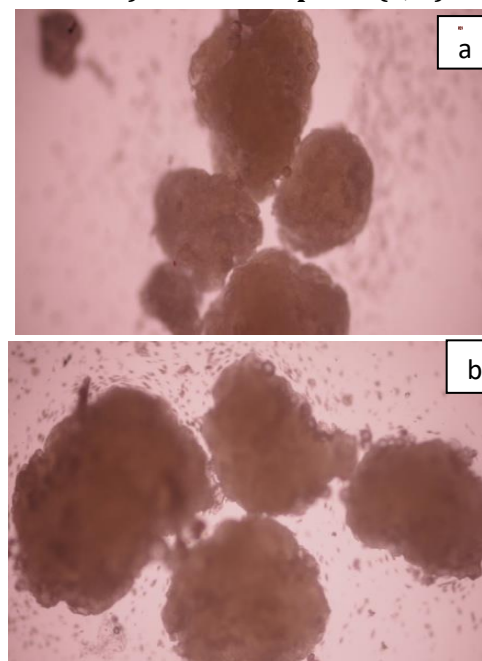


Figure 2. Optical images of synthesized (30 % DCOT) oil microcapsule (a, b).

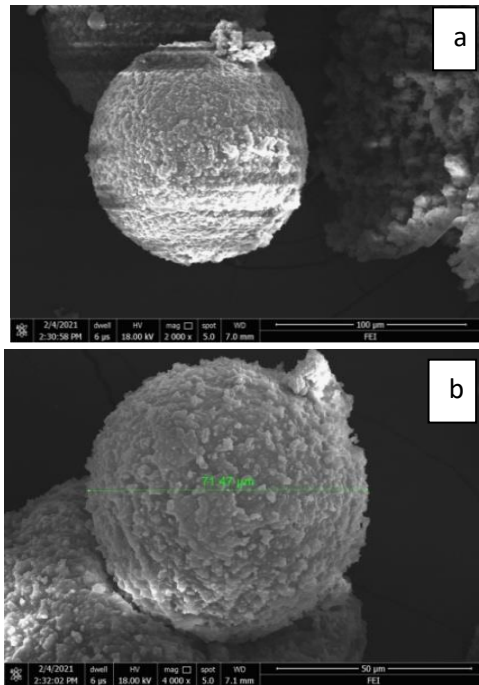


Figure 3. FESEM images of synthesized (20 % DCOT) oil microcapsules (a and b).

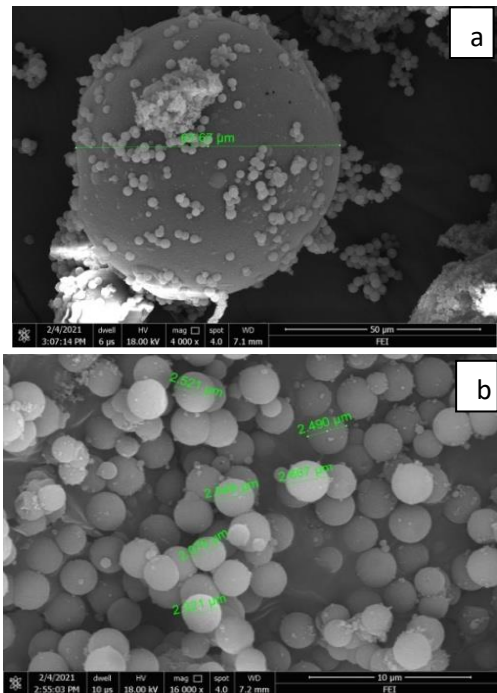


Figure 4. FESEM images of synthesized (30 % DCOT) oil microcapsules (a and b).

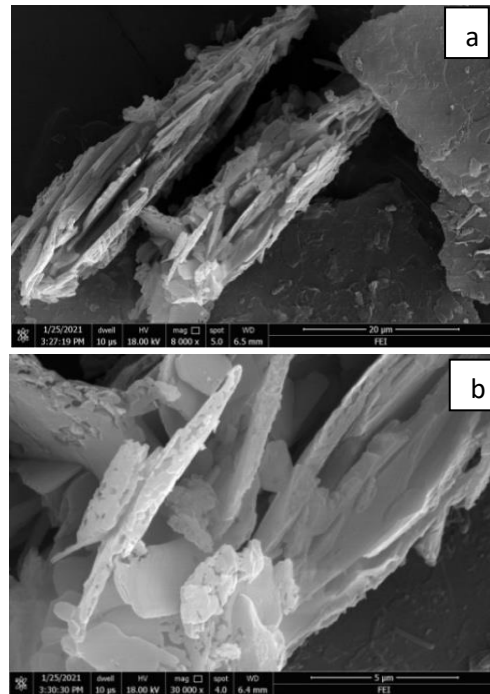


Figure 5. SEM micrograph of Polyaniline Nanoparticles (a, b).

Particle size analysis:

Particle size analysis of microcapsule evaluated with Malvern Mastersizer 3000 in aqueous dispersion medium. The particle size distribution of synthesized microcapsules shown in figure 6 and 7 is in the range of 0.77 μm to 2.42 μm. The particle size for 20 % DCOT oil has sauter mean diameter $D [3, 2]$ (SMD) value 1.39 μm and for 30 % DCOT microcapsule has SMD value 1.37 μm.

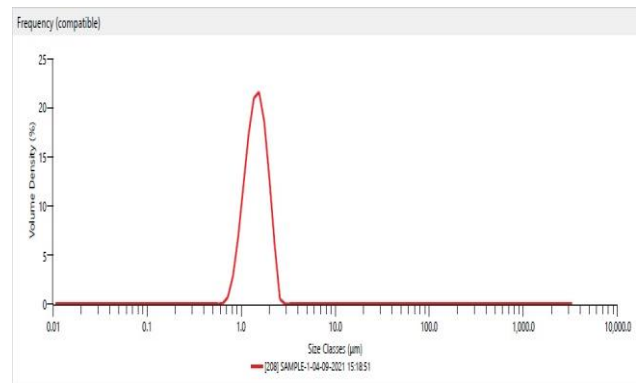


Figure 6. Particle size histogram of UF/Tung and Dehydrated Castor oil blend microcapsules (20 % DCOT)



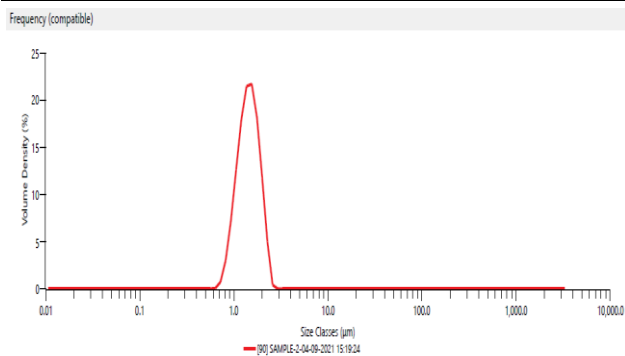


Figure 7. Particle size histograms of UF/Tung and Dehydrated Castor oil blend microcapsules (30 % DCOT).

Thermogravimetric analysis:

The weight loss with respect to temperature for DCOT oil microcapsules (20 and 30 %) are shown in Figure 8. The TGA analysis of 20. % DCOT and 30 % DCOT microcapsules shows three stage thermal decomposition. The first stage is in the range of temperature 20 OC to 100 OC due to evaporation of water. The second stage of thermal decomposition of microcapsules is in the range of 200 OC - 372 OC attribute to decomposition of crosslinked polymer and urea formaldehyde shell material. The encapsulated core DCOT oil blend decomposes at the temperature in the range of 376 OC - 540 OC.

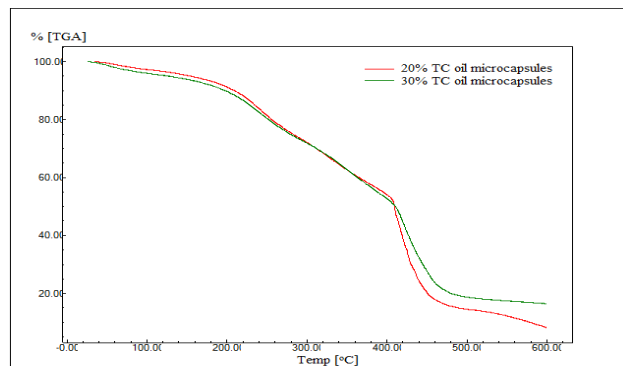


Figure 8. TGA curves of 20 % DCOT oil blend microcapsules and 30 % DCOT oil blend microcapsules

Oil content in microcapsule:

The amount of blended Tung and Castor oil in urea formaldehyde microcapsules was evaluated by extraction process using Soxhlet apparatus. It was found to be 33.6 and 40 % for 20 % and 30 % DCOT oil microcapsules respectively. The suitable amount of oil in microcapsules plays a

crucial role in self-healing process.

FTIR Analysis of PANI:

The Fourier transform infrared spectra (Figure 9) were precisely match with previously reported results. The characteristic bands at 1480 and 1583 cm⁻¹ attributed to C=N and C=C stretching frequencies for quinoid and benzoid rings. The bands at 1289 show C-N stretching of the secondary aromatic amine and the band at 691 cm⁻¹ represents aromatic C-H out of the plane bending vibrations. The broad band at 3000-3600 cm⁻¹ corresponds to the secondary stretching N-H vibration [29].

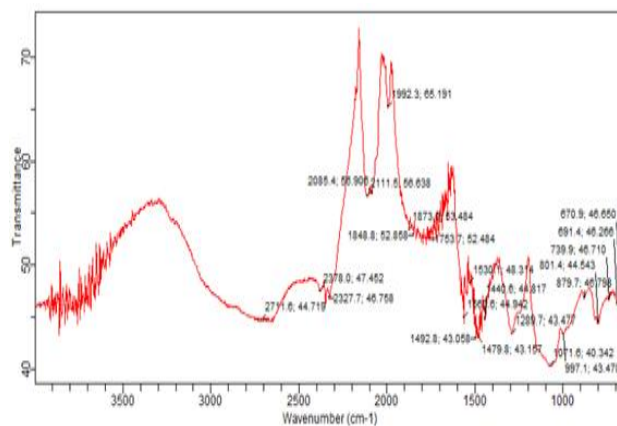


Figure 9. FTIR Spectra of PANI Nanoparticles

FTIR analysis of Microcapsules

The shell material and core content extracted from 20 % DCOT and 30 % DCOT microcapsules using Soxhlet apparatus were subjected for FTIR analysis. The FTIR spectrum of the extracted shell material of the 20 % DCOT (Figure 10) microcapsules showed closely matching characteristic bands with reported data [23]. The characteristic band observed at 3346 cm⁻¹ corresponded to N-H stretching vibration. The band observed at 1747 cm⁻¹ attributed to C=O stretching frequency. The band at 1458 cm⁻¹ attributed to C-H stretching vibration, while the band at 1219 and 1114 cm⁻¹ corresponded to C-N stretching vibration. The band at 769 cm⁻¹ attributed to the N-H wagging vibration [23]. The IR data confirmed shell material is made up of UF polymer.

The spectra of extracted core material of 20 % DCOT microcapsules (Figure 11) and 30 % DCOT microcapsules (Figure 12) have found closely



matching characteristic bands with the IR spectrum of blend of Dehydrated Castor oil and Tung oil (Figure 13). The characteristic band observed at 3026 cm⁻¹ shows stretching vibration band of unsaturated C-H group; the absorption band at 2924 and 2862 cm⁻¹ corresponded to the symmetric and unsymmetric stretching vibration; the band observed at 1745 cm⁻¹ for C=O stretching vibration; the band at

1452 cm⁻¹ attributed to C-H stretching vibration (angular deformation), while, the band at 1170 cm⁻¹ attributed to stretching vibration for C-O in ester. The bending vibration for -(CH₂)_n- group (n≥4) observed at 742 cm⁻¹. The FT-IR data clearly supported the encapsulation of Dehydrated castor oil and Tung oil blend inside UF shell material.

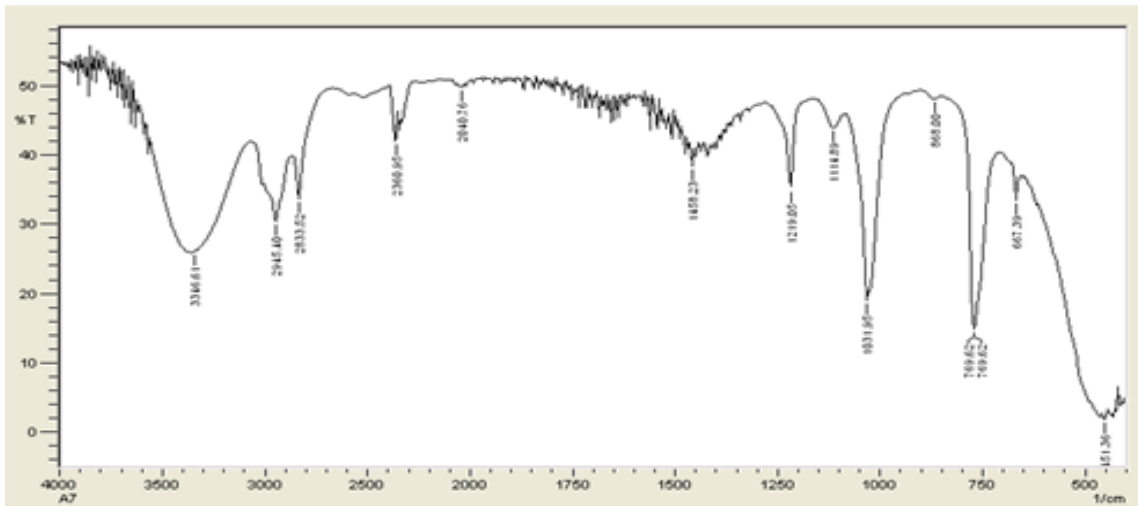


Figure 10. FTIR Spectra of shell material 20 % DCOT oil microcapsules

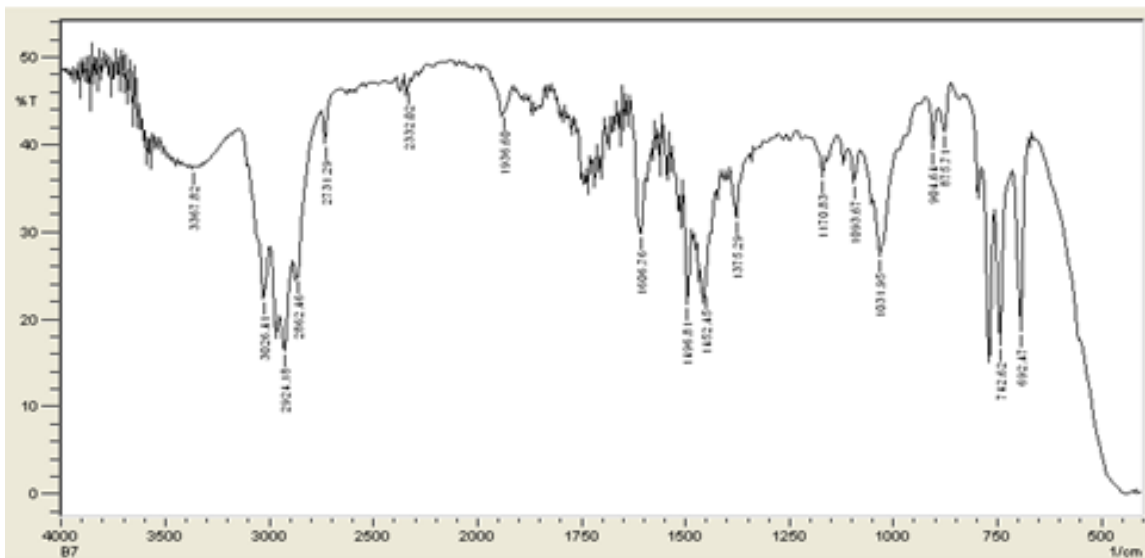


Figure 11. FTIR Spectra of extracted core material of 20 % DCOT oil microcapsules



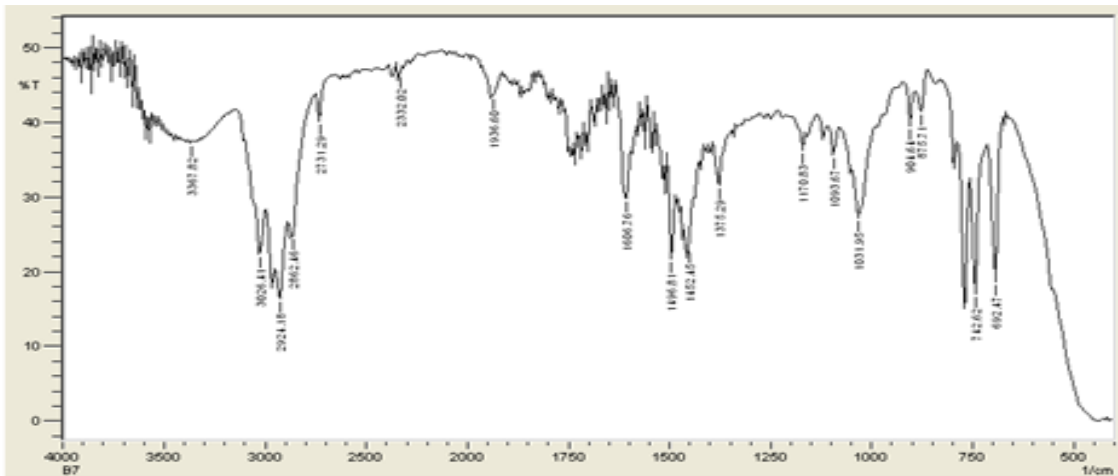


Figure 12. FTIR Spectra of extracted core material of 30 % DCOT oil microcapsules.

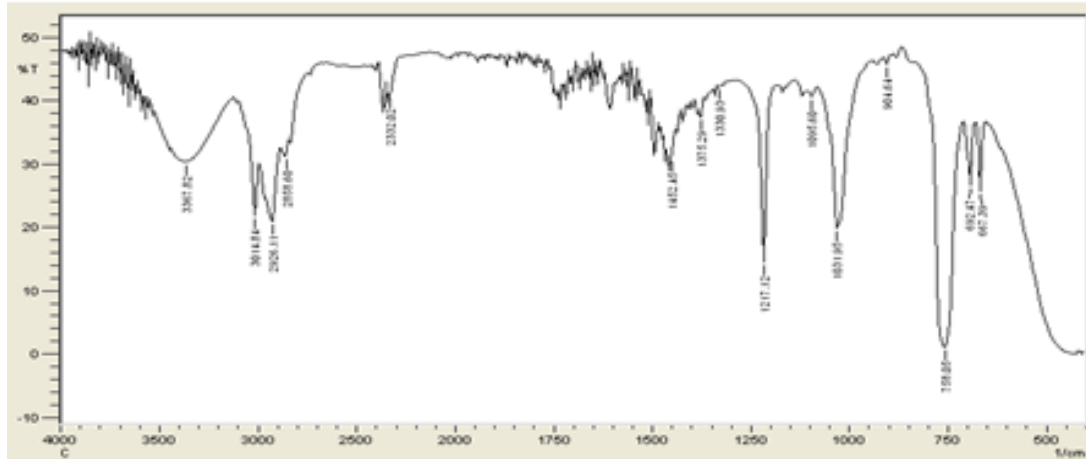


Figure 13. FTIR Spectra of neat DCOT oil (blend DCOT oil)

Oil content in microcapsule and control released study:

The content of blended Tung and Dehydrated Castor oil in urea formaldehyde microcapsule was determined by extraction process was found to be 33.6 and 40 % for 20 % and 30 % DCOT oil microcapsules respectively. The suitable amount of oil in microcapsules plays a crucial role in self-healing process. Percent of core material released

from microcapsules given in table 2 and 3 for 20 and 30 % DCOT. About 32.5 and 41.0 % core oil blend was released in 10 h from both type of microcapsule which are nearly same as the calculated from the formula of oil content of microcapsules. The core content of microcapsule plays an important role in the efficient self-healing of cracks as well as better corrosion inhibition.

Table 2. Extracted core material at different time intervals for 20 % DCOT

Weight of empty crucible (g)	Weight of empty crucible + Microcapsule (g)	Weight of Microcapsule (Core material+ Shell) (g)	Weight of released material	Time in hour	% of core material released
31.209	31.409	0.200	0.000	00	0.000
	31.375	0.166	0.034	2	17.0%
	31.367	0.148	0.052	4	26.0%
	31.350	0.141	0.059	6	29.5%
	31.346	0.137	0.063	8	31.5%
	31.344	0.135	0.065	10	32.5%



Table 3. Extracted core material at different time intervals for 30 % DCOT

Weight of empty crucible(g)	Weight of empty crucible + Microcapsule (g)	Weight of Microcapsule (Core material+ Shell) (g)	Weight of released material	Time in hour	% of core material released
24.372	24.572	0.200	0.000	0	0.000
	24.518	0.146	0.054	2	27.0 %
	24.510	0.138	0.062	4	31.0 %
	24.495	0.123	0.077	6	38.5 %
	24.491	0.119	0.081	8	40.5 %
	24.490	0.118	0.082	10	41.0 %

Physicochemical properties of coating matrix incorporated with microcapsules and PANI:

Gloss test

To disclose change in gloss due to the presence of 20 % and 30 % DCOT microcapsules and PANI nanoparticles in the coated panels. The gloss test was performed by using gloss meter (3nh) and the results are shown in table 4 and 5. The epoxy coating panels without microcapsules and 1 % PANI sample shows better gloss whereas, panels with 3, 5 and 7 % microcapsules showed steady decrease in gloss. This may be because of an increase in dullness in given coating with high composition of microcapsules.

Table 4. Gloss of the coated panel containing PANI and the different composition of 20 % DCOT microcapsules.

Sr. No.	Sample	Gloss %
1	Virgin	81
2	1% PANI	80
3	3%	72
4	5%	54
5	7%	52

Table 5. Gloss of coated panel containing PANI and different composition of 30 % DCOT microcapsules.

Sr. No.	Sample	Gloss %
1	Virgin	81
2	1 % PANI	80
3	3%	55
4	5%	70
5	7%	46

Evaluation of self-healing performance:

The self-healing ability of coating material was assessed and the healing performance of coating embedded with Dehydrated Castor oil and Tung oil studied by artificial scratches in epoxy coating matrix. The healing capability of coating matrix may be changes according to its surroundings, viscosity and temperature [26, 34].

A soon as the fracture generated in epoxy coating

results broken the microcapsules with a release of healing material (Figure 14) The released core material filled throughout the crack and starts healing process gradually (Figure 15). The released blended oil gets auto-oxidized forming free radicals with the formation of unsaturated pendent fatty acid, which enhances the viscosity of polymer result into the film formation [23]. In the present study, UF microcapsules containing Dehydrated Castor oil and Tung oil blend shows healing performance in epoxy coating to heal the crack.

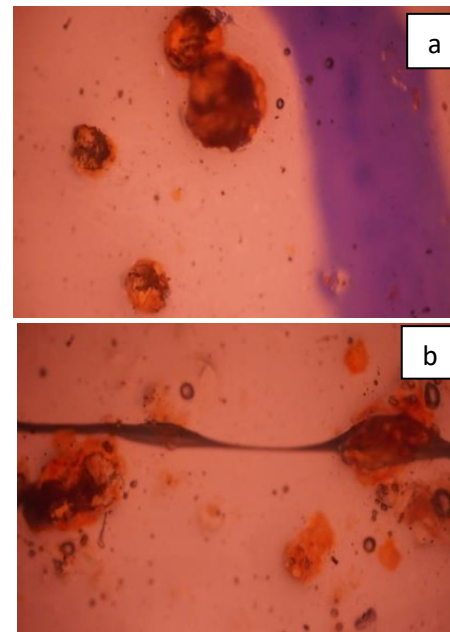


Figure 14. Optical Image of self-healing epoxy coating with microcapsule (a) released core of blended oil (30 % DCOT) filled through crack after artificial scratch (b).



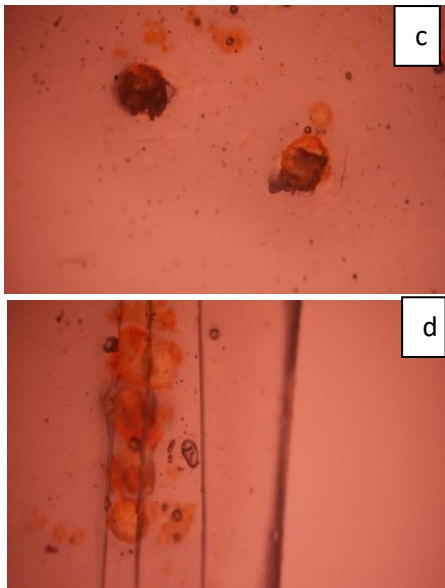


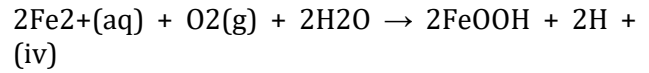
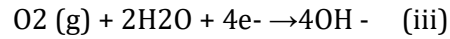
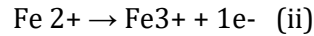
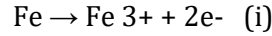
Figure 15. Optical Image of self-healing epoxy coating with microcapsule (c) released core of blended oil (20 % DCOT) filled through crack after artificial scratch (d)

Corrosion resistance of self-healing coating by immersion study

Corrosion of metallic surface is due to action of violent species like water, oxygen, ions etc. The coating acts as a barricade for such corrosive media. But whenever crack created within coating material, then moisture and oxygen get deposited over metal-coating boundary result into ionic impermeability of coating get suffered. The corrosion of carbon steel panel involves a number of redox reaction steps as given below.

Table 6. Control and self-healing coating compositions

Coating System	Microcapsules		Concentration of Microcapsules
	Core constituent	Shell material	
Control panel	-	-	-
With PANI	-	-	-
A	DCOT (30 % DCO)	UF	0
B (With PANI)	DCOT (30 % DCO)	UF	3%
C (With PANI)	DCOT (30 % DCO)	UF	5%
D (With PANI)	DCOT (30 % DCO)	UF	7%
E	DCOT (20 % DCO)	UF	0
F (With PANI)	DCOT (20 % DCO)	UF	3%
G (With PANI)	DCOT (20 % DCO)	UF	5%
H (With PANI)	DCOT (20 % DCO)	UF	7%



If any one out of these steps gets arrested anyhow, then corrosion gets inhibited. Whenever, coating will crack, microcapsules get rupture to release of healing material such as a drying oil and filled up the crack in coatings. Drying oil gets auto-oxidized at affected area by polymerization to form viscoelastic film [35]. Similarly, PANI acts a physical and chemical obstacle to the diffusion of corrosive media and reduced the corrosion rate by preventing the corrosive species from penetration to the steel panel surface. If coating become enough compact with strong adhesion onto metal surface, the penetration of corrosive species become difficult and at the same time the coating will show great performance [36]. Immersion study is an effective way to determine corrosion based on visible observation or physical changes on coated panel while, immersion in corrosive media.



In present study, immersion of coated panels in 0.5 M HCl (Figure 16) solution clearly showed that there was sacrifice of adhesion took place within one day for all samples and rapid corrosion seen for control specimen with 38 days immersion and has an extensive rust formation major within scratched area along with extending rust across the substrate surface. For the panel with PANI corrosion has been started after 65 days and for remaining panel system A to H (Figure 16) corrosion started from 78 days.

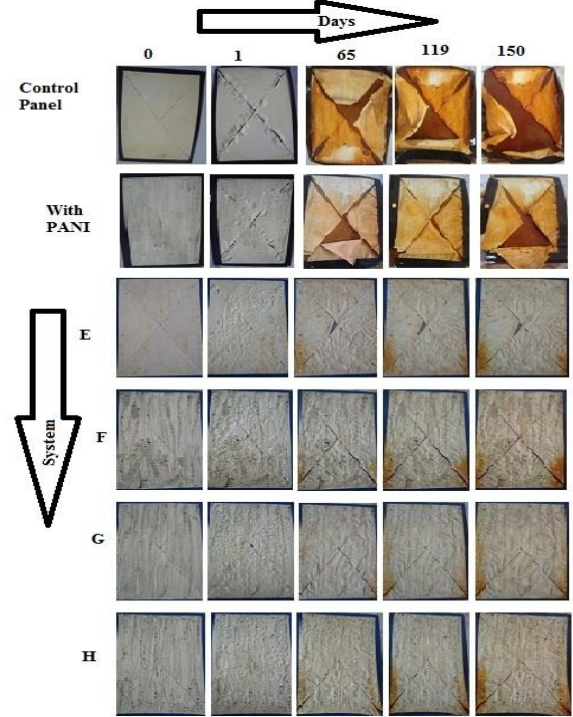
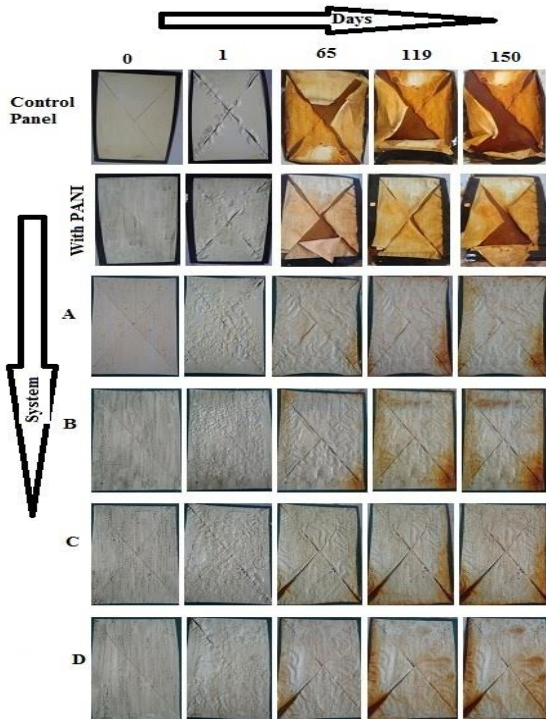


Figure 16. Control and different combinations of self-healing coating systems immersed in 0.5 M HCl solution.

The anticorrosive performance of the self-healing coating system immersed in 3.5 % NaCl (Figure 17) solution, the control panel started formation of burst within the groove of the scribed area from 42 days which increases further and started to corrosion from 127 days. For the system A to H (Figure 17) there was only starting of bursts from 42 day and further increases very slowly, but there is no start of corrosion up to 155 days.

From both the results of immersion study i.e., in acidic and salt media the multicore microcapsules and PANI nanoparticles might have played significant and crucial role for protection of corrosion of metallic surface with prototypical synergism of passivation and self-healing.

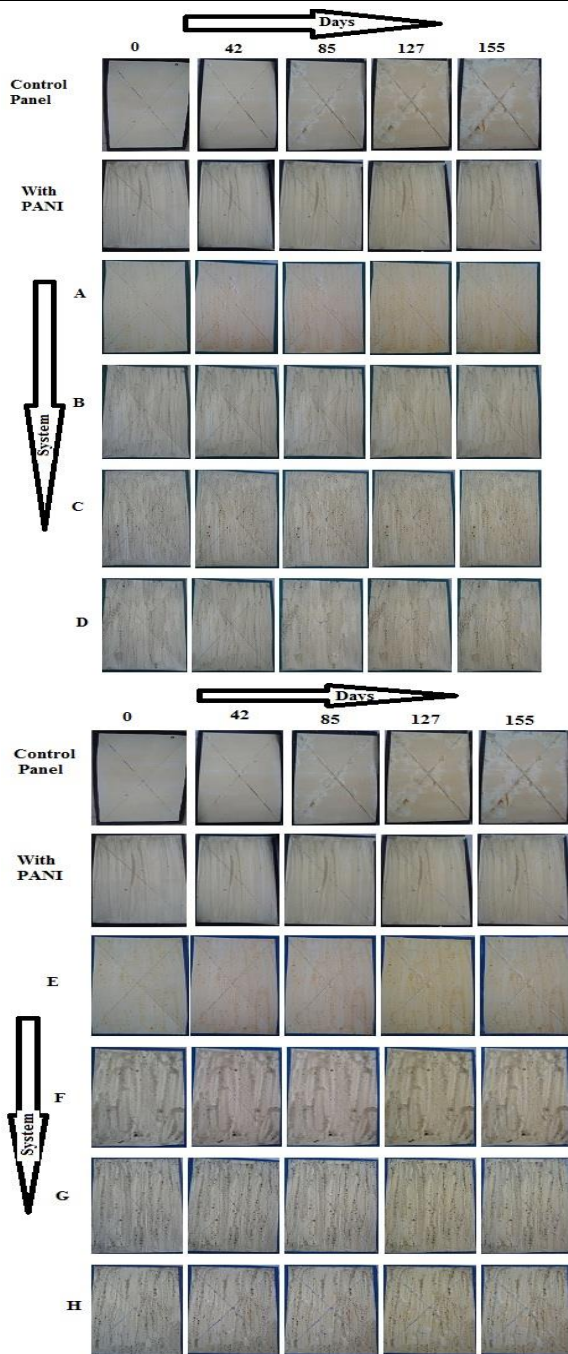


Figure 17. Control and different combinations of self-healing coating systems immersed in 3.5 % NaCl solution.

Conclusion:

Polyaniline nanoparticles were prepared by simple chemical deposition with single step polymerization method without any template or

acid. While, urea-formaldehyde microcapsules with blended Tung oil and Dehydrated Castor oil were synthesized by in situ polymerization technique. The morphology and particle size studied and verified by SEM, TEM, XRD, and FT-IR analysis. The synthesized microcapsule has a rough surface area and having good adhesion and distribution in coating matrix. The experimental study revealed that microcapsule incorporated along with PANI has effective anticorrosive property and self-healing ability in response to crack generated within coating, by filling the crack with oil and formation of viscoelastic film by air auto-oxidation.

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