ANTICORROSION PERFORMANCE OF SELF-HEALING POLYMERIC COATING ON LOW CARBON STEEL SUBSTRATES IN 3.5 wt.% NaCl MEDIUM

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Abstract. In this study, Poly-Urea-Formaldehyde (PUF) capsules containing linseed oil were prepared using in-situ polymerisation and 10 wt.% synthesised microcapsules were mixed into a commercialised epoxy paint. The linseed oil encapsulated poly-urea-formaldehyde (PUF) microcapsules had ∼85 wt.% core content with ∼200 µm diameter. Mass loss and corrosion rate measurements were used to investigate the impact of embedded microcapsules on the anticorrosive property of the self-healing coating. The complete self-healing coating had the excellent anticorrosive properties compared to epoxy coating without microcapsules. For defects such as micro cracks and porosity, the scratched self- healing coating demonstrated excellent healing ability as well as corrosion inhibition. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were used to investigate the failure of the scratched self-healing coating. The overall results and tests revealed that the self-healing coating has sufficient corrosion resistance when compared to the coating without microcapsules.

Keywords: low carbon steel, self-healing coating, microcapsule, linseed oil

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Introduction

The superiority of low carbon steel for various industrial requirements such as pipeline assembly, off/on shore structure, vessels, and tanks is due to its unique potential such as low cost, ease of welding, outstanding formability, and ease of accessibility [1]. Low carbon steel suffers from severe corrosion in marine environments, such as for oil and gas applications, during industrial processes and service. Hence, the industrial sectors take corrosion-prevention measures. Various techniques for corrosion control are used, including material selection, proper equipment design, and surface protection through coating, changing the metal electrode potential, and adding corrosion inhibitor [2]. While surface protection, such as coating, is one of the most cost-effective and practical strategies for preventing corrosive attack on metals in the maritime environment [2,3].

Polymer coatings and commercial paint are widely used to change the appearance of substrates, either for artistic purposes or to protect them from corrosion [4]. During its service and application, the paint coating undergoes mechanical property changes, resulting in the formation of micro-cracks, scratches, blasting, and other defects, which spread and expose the metal substrate to atmospheric moisture, chloride, sea water, and oxygen. This action causes increased disbanding or peeling of the coating, as well as flake formation from the substrate's coating interface [5]. Polymer coating can be thought of as a special class of pigments, special additives, composite materials, and binders. Later, the concept of self-healing cracks, which has been reported for composites, can be applied to coatings to provide longer durability. An attempt to heal scratches on oil and gas coatings using secret polymer properties has been reported [6].

The remarkable interest in self-healing coatings is most likely explained by their fascinating potential ability to recover their structural integrity autonomously after the occurrence of microcracks, which may occur due to the release of internal stress in a coating or mechanical damage. This type of functionality is expected to result in less maintenance and associated cost savings, which is especially appealing for offshore constructions like platforms and pipelines. Linseed oil, along with driers, was chosen as a healing agent in this study due to its ability to form films via atmospheric oxidation. In situ polymerisation was used to create microcapsules with urea–formaldehyde as the shell and drying oil as the core [8]. The effectiveness of these microcapsules in the healing of cracks in an epoxy coating as well as corrosion protection has been demonstrated.

The aim of this study is to develop self-healing coatings with microencapsulated linseed oil. In this study, microcapsules with urea–formaldehyde as a shell and linseed oil as a core were synthesized by in situ polymerization [2, 9, 12]. The efficiency of these microcapsules in healing of cracks or scratches area embedded in an epoxy coating was studied. Corrosion resistance of the scratched coatings on a low carbon steel substrate was studied via immersion test in 3.5 wt.% NaCl media as a verification of self-healing property for 7, 14, 21 and 28 days.

Materials and Methods

Table 1 shows the composition of the metal substrates used in this study, which is low carbon steel. A sheet of low carbon steel with dimensions of 20 × 20 mm and a thickness of 3 mm was laser cut. Only one side of the substrate material was coated with the investigated coating, while the otherside was coated with a layer of paraffin wax to prevent contact with the medium.

Table 1. Chemical composition (wt.%) of the substrates.

Alloy element	C	Si	Mn	P	S	Cr	Ni	Cu	Fe
Metal Substrates	0.174	0.176	0.624	0.0277	0.0212	0.104	0.0777	0.223	Balance

Surface preparation of the experimental coupons for corrosion test includes abraded with silicon carbide papers 80, 100, 300, 800, 1000 and 2000; rinsed with distilled water, sonicated for theremoval of polished residual particles in ethanol bath at room temperature for 20 min, dried and storedin a desiccator prior to use to prevent atmospheric corrosion.

Microcapsules were created using in-situ polymerisation in an oil-in-water emulsion. In a 1000 ml beaker, 300 ml of deionised water and 10 ml of a 5wt.% aqueous solution of polyvinyl alcohol (PVA) were mixed at room temperature. Under agitation, 5 g urea, 0.5 g ammonium chloride,and 0.5 g resorcinol were dissolved in solution. The pH was adjusted to about 3.5 by using a 5 wt.% solution of hydrochloric acid in deionised water. One to two drops of octanol were added as an antifoaming agent. 70 ml of linseed oil was added slowly to form an emulsion and allowed to stabilise for 15 min under agitation. After stabilisation, 12.67 g of 37 wt.% aqueous solution of formaldehyde was added slowly. The emulsion was covered and slowly heated and maintained at 55°C under stirring at 500 rpm for 4 hours. The contents were cooled at ambient temperature. Filtration under vacuum was used to recover microcapsules from the suspension. To remove the suspended oil, these were rinsed with water and washed with xylene [6-11]. The capsules were dried in a vacuum oven.

The linseed oil (LO) microcapsule was embedded in the epoxy matrix with a 10 wt.% selection. The epoxy and LO microcapsule were mixed at room temperature with slow agitation. Before it could be applied to the substrate material, the epoxy containing the LO microcapsule was continuously agitated for 30 min. The coating materials were then applied directly to 20 × 20 mm steel substrates using a brush paint application method. The coated specimens were left undisturbed for 7 to 14 days to dry and cure completely. Before the immersion test, all samples were cross- scratched. The purpose of the scratches is to see if the self-healing coating can heal or repair coating damage and protect the samples substrate better than pure epoxy coating.

Immersion testing was carried out in accordance with ASTM G1–03. All coated and uncoated specimens were immersed in a container containing 5 liters of 3.5wt.% NaCl medium for 7, 14, 21, and 28 days. After each immersion test, the samples were removed from the 3.5 wt.% NaCl solution and corrosion products were removed by soaking the samples. Before and after cleaning photos were taken for a visual inspection study. Afterwards, the samples were rinsed with distilled water, dried at high-pressure air, and weighed. The corrosion rate was calculated in the following manner:

$$\text{Corrosion Rate } (C_R) = \frac{K \times W}{A \times T} \tag{1}$$

Results and Discussion

Microcapsule properties. The size of microcapsules in self-healing coatings affects the amount of healing agent available for delivery to the cracked or scribed area. Figure 1 depicts the average diameter of the microcapsules, which ranges from 180 to 250 µm. The amount of microcapsule added was approximately 10 wt.% of the total self-healing coating material. According to a previous study by Hatami *et al.* [12], the optimum concentration of microcapsules is 10 to 20 wt.%, because when the concentration of microcapsules is too low, the healing agent delivered to the damaged region is insufficient, whereas when the concentration of microcapsules is too high, the coatings porosity increases and density decreases, which promote to poor water resistance.

SEM micrographs reveal more information about the sub-micron derbies and features on thesurface of the microcapsules (Figure 1). These microcapsules were relatively spherical in shape, witha rough and non-porous exterior shell wall similar to [12-13] studied. The rough morphology of the microcapsules ensured good mechanical bonding to the coating matrix. Their spherical shape ensuredthe capsules' storage function as well as their easy dispersion into the coating. As discussed by Benzab*et al.* [10], the surface morphology of microcapsules is highly dependent on the core material properties (e.g., viscosity, surface tension, miscibility with shell material, etc.), core:shell ratio, and microencapsulating process [3,10]. Figure 1(c) shows the EDS spectrum of a linseed oil (LO) microcapsule, which contains carbon, nitrogen, and oxygen due to the composition of linseed oil and poly-urea formaldehyde (PUF) as the shell of the microcapsule. Figure 1(d) depicts the visual appearance of a microcapsule after one week of filtration and drying.

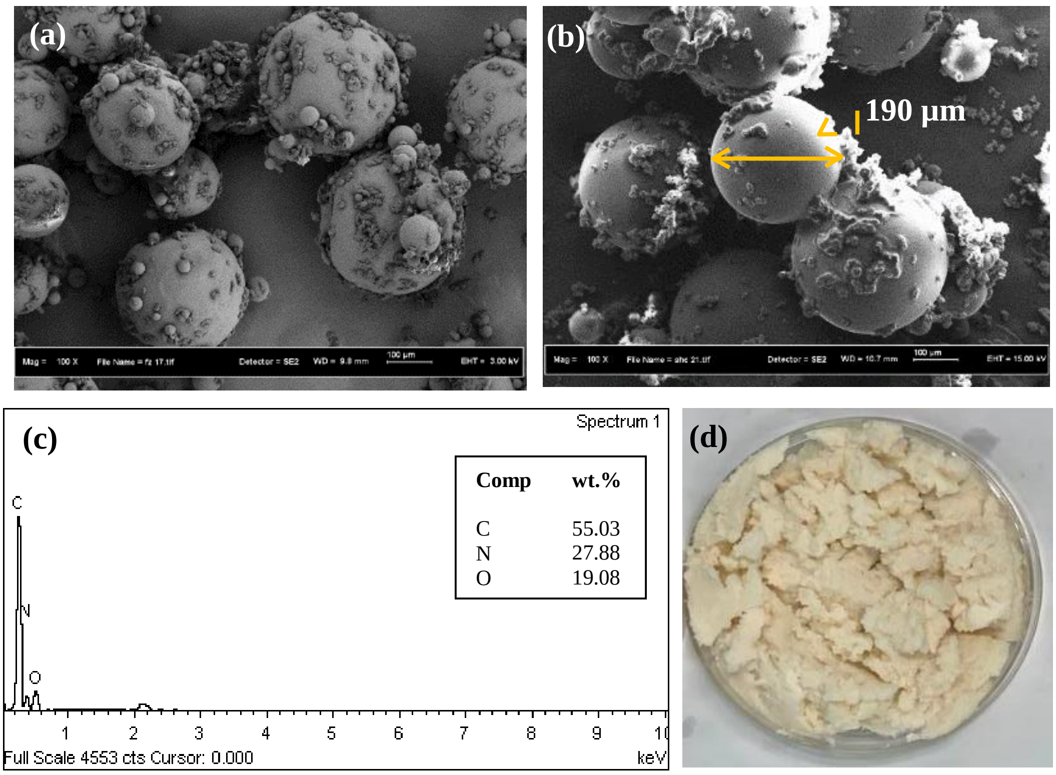
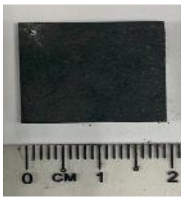
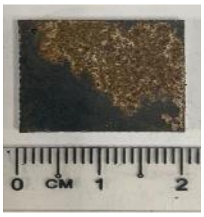
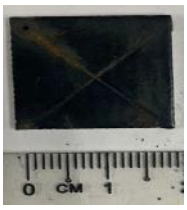
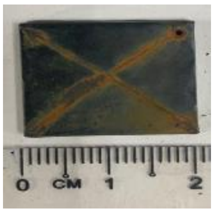
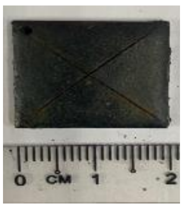
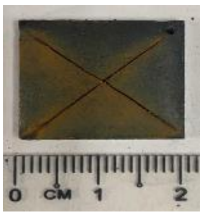
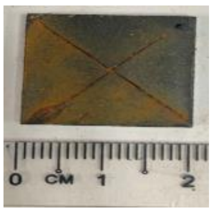


Figure 1. FESEM micrograph for (a) Microcapsule of Linssed oil after synthesis, (b) Final size ofmicrocapsule, (c) EDS spectrum of (b) and (d) Physical microcapsule after filtration

Visual Inspection after immersion test. The immersion test was performed for 7, 14, 21, and 28 days to investigate the corrosion behaviour of the self-healing microcapsule embedded in epoxy coated samples. Table 2 shows that the uncoated sample suffers or has very poor corrosion protection because there is no protection, and it is completely lost. Following that, a corrosion product appeared on the epoxy coated sample that did not contain a microcapsule. This indicates that chloride ions, water, oxygen, and other substances were able to pass through the plain epoxy coating, resulting in corrosion on the steel substrate material.

However, due to the healing agent's excellent ability to heal the damaged region, there is almost no corrosion product observed on the self-healing coated sample after 7 days of immersion testing. According to the visual observation results shown in Table 2, the corrosion products were mostly found on the epoxy coated without microcapsule samples. Table 2 shows that no delamination, blisters, peeling, or cracking defects were observed in either coated sample [10-15]. While there wasless corrosion product visible on the surface of the LO microcapsule embedded in the epoxy self- healing coated sample.

Table 2. Sample after immersed in 3.5wt. % of NaCl solution.

Duration of Immersions (days)	**7**	**14**	**2 1**	**28**
Without Coating				
Coated with Epoxy				
Coated with Self-healing Microcapsule				

Based on visual inspection after 14 and 21 days of immersion in 3.5 wt.% NaCl medium, it was discovered that the amount of corrosion product on the surface of epoxy coated without microcapsule samples increased when compared to self-healing coated samples. The amount of corrosion product observed on the self-healing coating, on the other hand, indicated that some areas were not fully protected with the healing agent. When compared to the self-healing coated samples, the amount of corrosion product was mostly found on uncoated and epoxy-coated samples after 28 days of immersion. Corrosion products were also formed on the self-healing coated samples because chloride ions were able to break the unprotected area of the coating after prolonged exposure and the microcapsules were unable to heal the coating surfaces.

Mass loss and Corrosion rate measurement. Figure 2 shows the overall mass loss measurements of the immersion test and corrosion rates. According to previous research [2, 9, 12] the outstanding anticorrosion function of self-healing coatings on steel substrates is due to the released healing agent from ruptured microcapsules, which can seal and heal the damaged area automatically.

Figure 2(a) demonstrates that as the immersion period increases, the weight loss for the epoxy coated without microcapsule samples increases. On the other hand, the self-healing coated samples increase initially but begin to diminish after 28 days of immersion test. Since the self-healing coated samples began to repair or heal the damaged coating by releasing the LO microcapsule, the sample was protected from further corrosion. Even though the amount of weight loss reduces with time, the corrosion product was still visible on the samples after prolonged contact because not all the microcapsules are released from the coating because it is depending on the crack location, crack size, and the enough linseed oil to heal the crack.

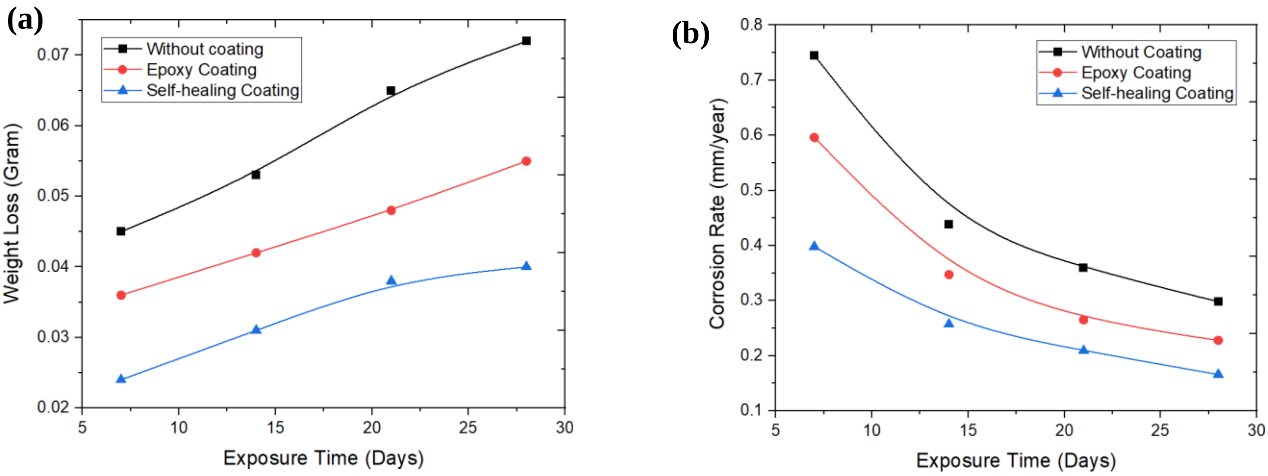


Figure 2. Immersion test results after 7, 14, 21 and 28 days for (a) Weight loss and (b) Corrosionrate measurement for uncoated, epoxy paint and self-healing coating in 3.5 wt.% NaCl medium

Figure 2(b) presents a general decrease in corrosion rate. The chloride ions in the 3.5 wt.% NaCl medium would be depleted after a period of time, as a result, the corrosion process was slowed. Furthermore, the formation of corrosion products on the samples' surfaces acted as a corrosion barrier. The epoxy without microcapsule coated samples have a higher corrosion rate than the self-healing coated samples because the epoxy coating that attacked by the corrosive solution was not restored, causing the samples to corrode. Meanwhile, corrosion process was slowed in self- healing coated samples that were covered by a layer of LO microcapsules embedded in the epoxy coating, particularly in the scribed region. When the coating was ruptured during the corrosion attack, the linseed oil was released from the microcapsule. The underlying steel substrate sample would be protected from further corrosion once the coating was repaired or healed. As a result, the corrosion rate of self-healing coated samples is lower than epoxy samples without microcapsules coated samples. Hatami Boura *et al*. [12] found that after 1, 7, and 21 days, the corrosion resistance of epoxy coatings in a 3.5 wt.% NaCl solution decreased as the immersion time increased.

Surface study by SEM/ EDS. Prior to the corrosion test, an initial test was performed to determine whether the self-healing coating would function properly. A cross scratch was made on the self-healing coated sample, which was then left in a normal environment at ambient temperature for seven days. Similarly, for control and comparison purposes, the same was done on epoxy paint samples that were not microcapsule coated. The samples were then analysed using SEM, and the results are shown in Figure 3. Figure 3(a) depicts an open scribed region for pure epoxy paint that reveals the steel substrates, as in the [15-17] studies. The open area size of ~ 257.8 µm promotes corrosion behaviour. While, for self-healing coating, the microcapsules embedded in the epoxy were ruptured or broken and released the healing agent, linseed oil, which healed the scratch area as shown in Figure 3(b) after 14 days and the size of the scribed area was reduced to ~ 95.97 µm to protect the metal substrates. Figure 3(c) demonstrates the performance after 28 days of exposure to 3.5 wt.% medium completely protected with the size ~ 55.53 µm.

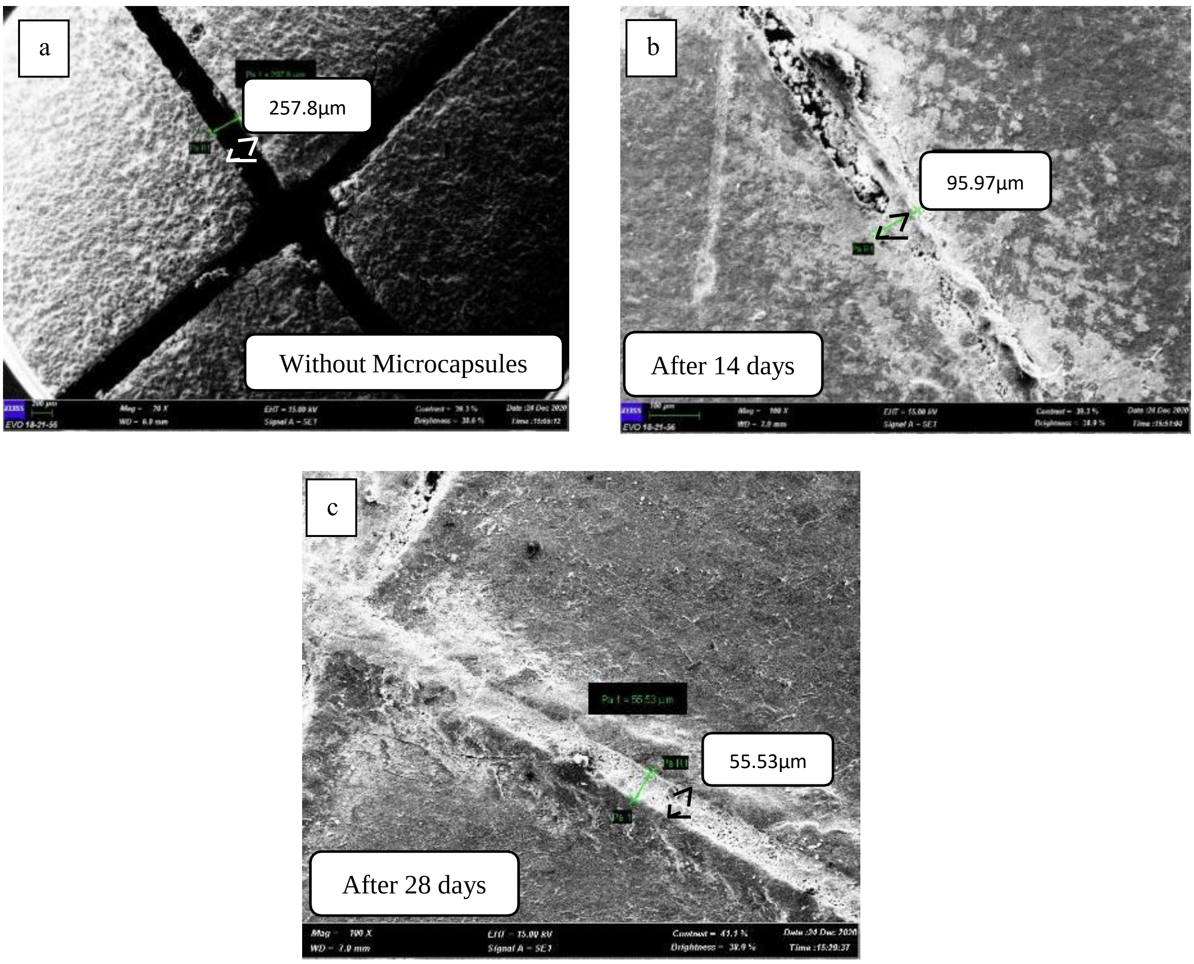


Figure 3. SEM micrographs of (a) samples without microcapsules, (b) self-healing coating after14 days in 3.5wt.% NaCl, and (c) self-healing coating after28 days in 3.5 wt.% NaCl.

The discussion by Huang M. *et al.* [13] is based on several assumptions, including: (a) that microcapsules with uniform diameter are evenly distributed in the epoxy paint coating matrix; (b) that the fill content of each LO microcapsule is the same; (c) that the shell of the microcapsules is negligible; and (d) that when a scratch or crack forms in the coating, all of the microcapsules locatedat the scratch plane are ruptured; (e) all of the encapsulated healing agent of ruptured microcapsules will freely flow into the scratch; (f) the healing species will spread within the scratch [13].

Figure 4 depicts a SEM micrograph and an EDS spectrum for epoxy paint without microcapsules and self-healing coating after a 28-days of immersion test. In general, the healed area'scomposition matched that of the microcapsules, as shown in Figure 4 (b and d). Figure 4 (a and b) shows that the healing agent or inhibitor was released into the scratch region after the damage occurred, and that the mixture of epoxy paint and linseed oil composition consists of O, C, Mg, Si, and Fe [16, 17]. Figure 4 (b and d) show the EDS spectrum, which consists of O, Na, Mg, Si, and Fe. The important composition is Fe, which shows that the epoxy paint without microcapsules has a higher value to simulate an unprotected area at the scribed area, while Figure 5 (d) shows a lower amount of Fe initially protected by linseed oil rupture at the scribed area.

As a result, the coating demonstrated good self-healing properties while also protecting the substrate. According to Suryanarayana *et al.* [9], the effective self-healing coating occurs when the microcapsules incorporated in the paint film break immediately to release healing material when cracks in the paint film are generated. It has also been discovered that the shell surface of microcapsules is very rough, which will allow for good bonding with the film matrix [9,17].

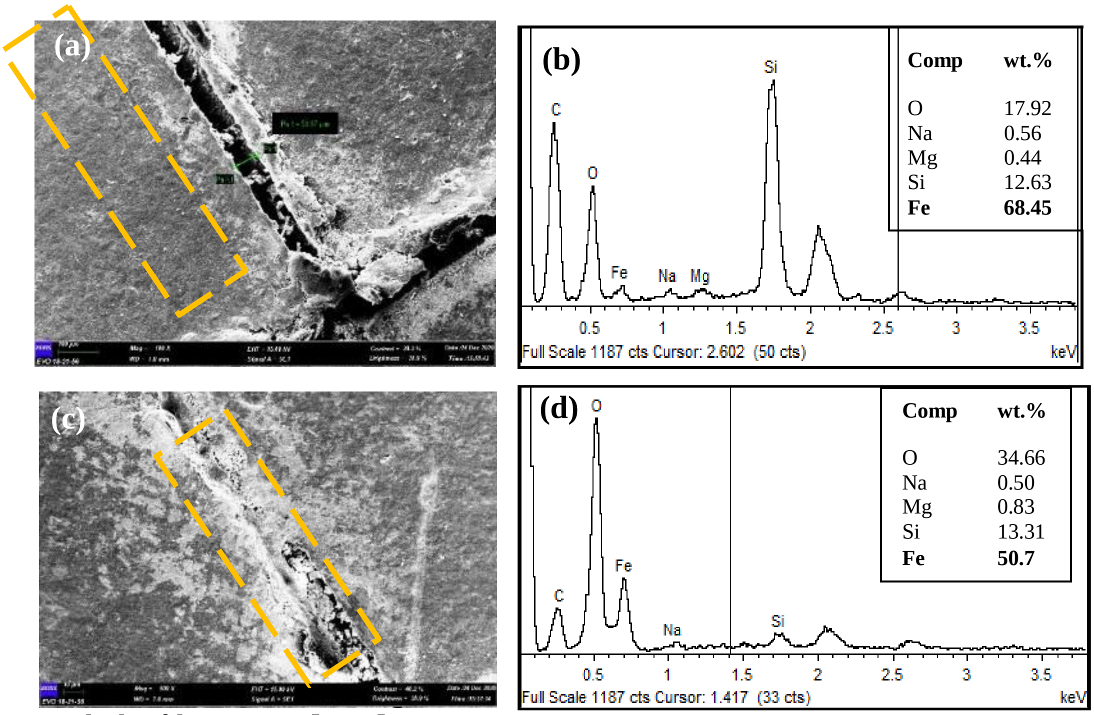


Figure 4. SEM micrograph and EDS spectrum for samples after 28 days exposure in 3.5wt. % NaCl solution (a) Epoxy without microcapsules, (b) EDS spectrum of area (a), (c) Self-healing coating and (d) EDS spectrum of area (c).

Conclusion

1. In this study, the PUF microcapsules containing linseed oil were successfully synthesized via in-situ polymerisation method. This study demonstrated the potential for developing self- healing anticorrosion coatings by incorporating 10 wt.% microcapsules concentration into commercialised epoxy paints.

2. A successful release of the linseed oil from the capsules embedded in the epoxy coating uponmechanical damage was confirmed by SEM image and EDS spectrum. During the immersion test of the anticorrosion performance of the self-healing coating, the microcapsules ruptured and released the linseed oil draying oil material, which efficiently healed cracks with satisfactory anticorrosive properties throughout mechanical damage.

3. As a result, this coating significantly improved the anti-corrosion performance and decreased the corrosion rate of the coated low carbon steel substrates. The self-healing coating has a good ability to repair damage that occurs on the coating of a steel substrate by releasing the healing agent in the microcapsules embedded in the epoxy matrix and sealing the exposed area from further corrosion.

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Author Contributions

All authors contributed toward data analysis, drafting and critically revising the paper and agree to be accountable for all aspects of the work.

Disclosure of Conflict of Interest

The authors have no disclosures to declare.

Compliance with Ethical Standards

The work is compliant with ethical standards.

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