

ANTICORROSION PERFORMANCE OF SELF-HEALING POLYMERIC COATINGS ON LOW CARBON STEEL SUBSTRATES

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Graphical abstract



Abstract

Recently, self-healing coating is classified as one of the smart coatings which has the ability to heal or repair damage of the coating to prevent further corrosion. The aim of this study is to synthesize the self-healing coatings from polymeric material and evaluate the performance and their corrosion behavior when coated on steel substrates. The corrosion tests were performed using immersion test and salt spray test method at room temperature. The immersion test shows that self-healing coating gives lower corrosion rate compared to pure epoxy paint, with a value of 0.02 and 0.05 mm/year respectively. Also, salt spray test shows similar trend as the immersion test, which is 0.11 and 0.19 mm/year for self-healing coating and pure epoxy paint respectively. While uncoated samples without any protection corroded at 0.89 mm/year. It was also found that the damage on self-healing coating was covered with zeolite from the microcapsules indicating that the self-healing agent was successfully synthesized and could function well. In other words, self-healing coating shows better corrosion resistance compared to the pure epoxy coating on steel substrate.

Keywords: Self-healing coating, Zeolite, Microcapsule, Low carbon steel, Corrosion resistance

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1.0 INTRODUCTION

Corrosion problem on metallic materials has been a worldwide issue, which may lead to higher overall cost, economic loss and severe structure failure. The application of polymer or composite and organic coatings are widely used for the protection of bare metal surfaces against corrosion in petrochemical and oil and gas industry [1-5]. The characteristics and performance form as barrier for the corrosive environment such as marine, providing the simultaneously protection, they may serve as a matrix for anticorrosive performance and as passive layer for

active anticorrosive action at the metal surface [1, 3, 5]. As prevention application of polymer or paint coatings is the most common method for corrosion protection on steel substrates because easy to applied and low cost. However, polymer or paint coatings are subjected to mechanical damages, such as micro-crack, scratches and cuts, which may cause failure of coatings and subsequently, water (etc. salt water) would penetrate through the coating to metal substrates and immediately cause corrosion. Therefore, the concept of the self-healing coating has been proposed to act as a quick remedy for mechanical damages to extend the coating service application [4-7].

Self-healing coating that autonomous crack repairs and major improvements of polymeric coating application in on/ off shore structure, petrochemical and oil and gas industry [1, 2, 5-9]. The main aim is to develop materials with a built in capability to restore their structural integrity autonomically after the damage and retain functionalities [1-7]. Generally the capsule-based, vascular, and intrinsic materials are three most studied approaches or strategy in recent study on self-healing materials [5]. Among them, micro/nano capsule-based materials have been adopted frequently and command for developing self-healing coatings strategy [3-7].

The new concept of self-healing in polymeric was introduced thorough combination with green inhibitor compounds directly into the polymer matrix such as zeolite, chitosan and etc due to the high toxicity of commercial inhibitor [1-7]. The mechanism of action of green inhibitors is not fully understood, however, the adsorption properties are expected to explain their anticorrosion effect [3-8]. The successful of encapsulation process of the inhibitor inside microcapsule that prevents the interaction of the inhibitor with the polymer matrix and provides the self-healing properties [3, 9].

Recently, *in-situ polymerization* is the best process and easiest to encapsulation method, because it does not require high level technology compared to other methods [10-13]. The issue is healant material phase is whether liquid or powder, must be able to flow freely through the crack region [10]. The efficiency of a self-healing corrosion protection coating system using Poly(urea-formaldehyde) (PUF) microcapsules containing several types of film forming compounds (healants) and corrosion inhibitors has been reported [14-18]. Zeolites have been used in many applications because of their unique properties and environmentally friendly [19]. Generally, zeolites have large ion exchange capacities and incorporation with metal ions will improve their antibacterial properties [19]. Therefore, by treatment thorough functionalization of zeolite has excellent antibacterial and fungal properties and also promotes the adhesion and interaction with negatively charged bacteria and improves its biocidal activity and suitable application in marine application [19, 20].

Epoxy paint or resin are reactive monomers and can be quickly cured with wide variety of hardeners such as amines [23]. Recently, they have a wide range of applications such as surface coating, for oil and gas industry due to the excellent mechanical resistance of the cured products and good adhesion to many substrates [23, 30-32]. However, during the applications, epoxy polymer still has some disadvantages such as brittleness and easy to crack [23, 32]. Thus, research which are focused on properties improvement with addition of micro/ nanoparticles can significantly improve the mechanical properties and anticorrosion performance [32-33]. Therefore, epoxy paint or resins should be a good candidate as coating matrix for the fabrication of self-healing coating embedded with various types of microcapsule agents [23, 34].

As evident from the literature survey, the performance of self-healing coating and functionalized zeolite have great potential and advantages in corrosive environments as in the marine, petro-chemical and oil and gas industries. The present study explored the functionalized zeolite as a healing agent due to anticorrosion properties were synthesized by *in situ polymerization*. As the result the efficiency of microcapsules in healing of scribe regions in an epoxy paint and corrosion protection has been demonstrated.

2.0 METHODOLOGY

2.1 Preparation of Substrates

The metal substrates used for this study is low carbon steel and its composition is given in Table 1. A sheet of low carbon steel with 20 x 20 mm size and 10 mm thickness was cut using EDM wire cutting machine. Only one side covered with the investigated coating, while other side of the substrate material was coated with a layer of paraffin wax to avoid any contact with the medium.

Table 1 Chemical Composition (wt. %) of the low carbon steel used

C	Mn	Ni	Cu	Si	Fe
0.031	0.273	0.046	0.016	0.0097	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 the removal of polished residual particles in ethanol bath at room temperature for 20 min, dried and stored in a desiccator prior to use to prevent atmospheric corrosion.

2.2 Preparation of Coating Material

2.2.1 Functionalization of Zeolite

The zeolite must be functionalised in order to make it active ingredient. This was done as follows: 4g of natural zeolite was mixed with 100ml of concentrated sulphuric acid. The mixture of zeolite and concentrated sulphuric acid was ultrasonicated for 4 hours at room temperature. After that, the mixture was stirred for 6 hours at 80°C by using magnetic stirrer. This is to ensure that complete absorption of the acid. After finish stirring for 6 hours, 1.0L of distilled water was added slowly by using burette to reduce the acid absorption. Then the solution was filtered by using filter paper. It was washed with acetone and distilled water. Finally the product that has been filtered was dried in the oven for 24 hours at 60°C. The final product which was functionalized zeolite was in the powder form.

2.2.2 Synthesis of Microcapsules

After completion of making the zeolite functionalized, the microcapsules were prepared before embedded in epoxy. First, the mixture which consists of 0.5 g ammonium chloride, 5g urea and 0.5g resorcinol was prepared. Then the mixture was added into a flask with 200ml deionized water at room temperature (27°C). The solution was kept pH at 3.5 by adding hydrochloric acid solution and 3.6wt% deionized water. Next, 4g of zeolite that has been functionalized was added slowly into the solution with pH 3.5. The solution was allowed to stabilize for 10 minute. Then 12.67 g of 37 wt. % aqueous solution of formaldehyde was added into the solution in a flask. When 37wt% aqueous solution was added, it was put under a bath of water with controlled temperature measured with an external temperature probe. The solution was then being stirred at 700 rpm for 4 hours at 60°C. After that the solution was filtered by filter paper and washed with deionized water. The product that has been filtered was dried and the product was in powder form.

2.3 Coating Process

The microcapsule of zeolite was embedded in the epoxy matrix with a ratio of 1:9 which is 1 is the zeolite powder that has been embedded in microcapsule and 9 is the epoxy matrix. The epoxy and microcapsule of zeolite were mixed together under slow agitation at ambient temperature. The epoxy that contained the zeolite microcapsule was continuously agitated for 30 minute before it can be applied to the substrate material. Then, the coating materials were directly applied onto 20 x 20 mm steel substrates using the brush paint application method. The coated specimens were kept undisturbed for 7 to 14 days to allow complete drying and curing. A cross scratch was made on all samples before the salt spray test was conducted. The purpose of the scratches is to determine whether the self-healing coating can heal or repair the coating damage which can protect the samples substrate better than pure epoxy coating.

2.4 Corrosion Test

2.4.1 Immersion Test

Immersion test is the common test to evaluate the corrosion rate of a sample substrate by weight loss method. The immersion test was performed based on ASTM G31 – 24 [21] which is the standard guide for immersion corrosion testing of metal. A total of twelve samples of low carbon steel substrates with size 20 x 20 mm were prepared. The samples were divided into two groups; the first group was coated with pure epoxy paint and the second group of samples were coated with epoxy embedded with zeolite microcapsules. All samples were immersed in the 3.5wt% of NaCl medium for eight weeks. For visual inspection, photos of the samples before and after cleaning were taken. After

the corroded samples have been cleaned, the samples were reweighed and weight loss was calculated from the difference of weight before immersion and weight after immersion. At the end of the eighth week, the final corrosion rate was calculated using Equation (1).

$$\text{Corrosion rate (mm/year)} = \frac{(K \times W)}{(A \times T \times D)} \quad (1)$$

where K is a constant of 8.76×10^4 , W is the mass loss in g, A is the area exposed to corrosion in cm^2 , T is the time of exposure in hours and D is the density of low carbon steel in g/cm^3 or 7.85 g/cm^3 .

2.4.2 Salt Spray Test

The salt spray test was conducted in accordance to ASTM B117-11 [22] which is the standard practice for operating salt spray apparatus. The exposure time for the salt spray test was 3, 7, 10 and 14 days. During the test, the chamber of the salt spray was kept at 35°C and at pressure of 8psi. Before being exposed to the salt spray, the weight of the samples was measured. The samples were placed on a polystyrene holder at an angle of $15\text{-}30^\circ$ from vertical which allowed condensation to run down the specimens and to minimise condensation pooling [22]. After the test has been completed, photos of the samples after the salt spray test were taken. The weights of samples before and after the salt spray test were recorded. The average corrosion rate could be obtained, using equation (1).

3.0 RESULTS AND DISCUSSION

3.1 Self-Healing Performance

The overall sizes of the microcapsules range from 50 to $65 \mu\text{m}$ after final synthesis. The amount of microcapsule added was about 20wt. % of the total self-healing coating material. Similarly from the previous study by Xiuxiu et al. [23] reported that the optimum concentration of microcapsule is 20wt. %, because the healing agent delivered to the damaged region is inadequate when the concentration of microcapsules is too low, while increases the coatings porosity and reduces their density when the concentration of microcapsules is too high, which will lead to their poor water resistance. Steel substrate samples were coated with pure epoxy and encapsulated zeolite self-healing embedded in epoxy as presented in Figures 1 (a) and (b) which shows the thickness measurement taken at cross sections of both samples.

Figure 1 clearly shows the pure epoxy coating average thickness of $108 \mu\text{m}$. The zeolite microcapsule embedded in epoxy coating shows higher thickness range, with an average $178 \mu\text{m}$. This may be due to the presence of the microcapsules in the epoxy coating that makes it thicker than the pure epoxy coating and the range of thickness was similar with [23, 25, 28]

studies. Both coating materials were applied by brushing with the same number of strokes.

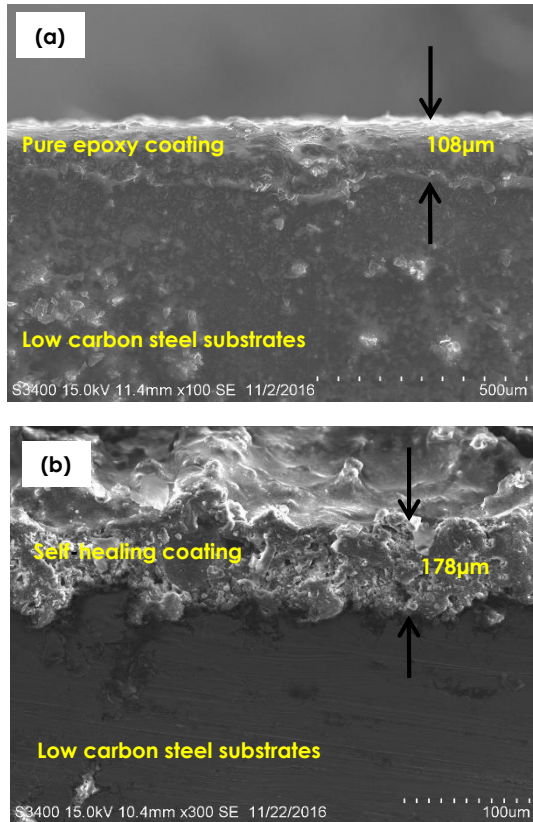


Figure 1 VPSEM image thickness of coating from the cross section area for (a) pure epoxy and (b) self-healing coated sample

An initial test was conducted to show whether the self-healing coating would function prior to corrosion test. A cross scratch was made on the self-healing coated sample and was left in normal environment at ambient temperature for seven days. Similarly, the same was done on pure epoxy coated sample for control and comparison purpose. The samples were then analysed using VPSEM and the results are shown in Figures 2 (a to c). Figure 2a shows the open scribed region for pure epoxy paint revealing the steel substrates similar with [16, 24] studies. While, for self-healing coating the microcapsules embedded in the epoxy was ruptured or broken and released the healing agent which is zeolite and healed the scratch area as presented in Figure 2b on first day and Figure 2c after seven days exposure to ambient temperature.

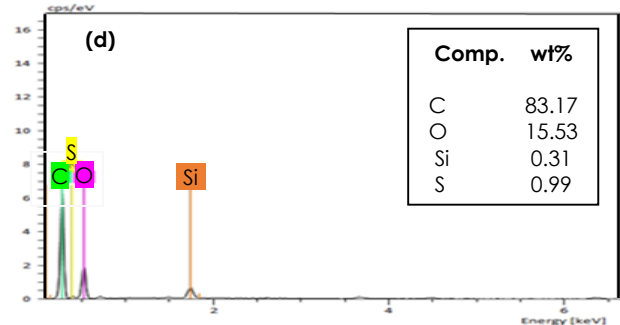
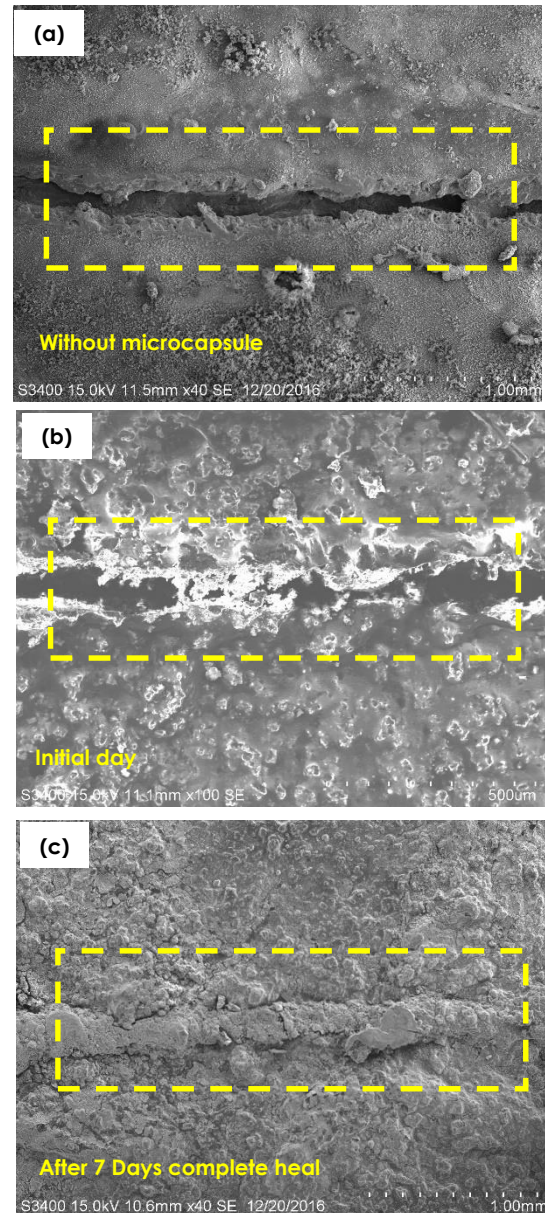


Figure 2 VPSEM surface morphologies of (a) pure epoxy paint, self-healing epoxy coated sample (b) initial scratch was introduced, (c) image of sample after one week exposure in air and (d) EDX analysis of scribed region (c)

The composition of the healed area was similar to the composition of the microcapsules as shown in Figure 2 (d). The mixture of epoxy paint and zeolite composition consists of O, C Ni and Si, that shows the healing agent or inhibitor were released into the scratch region after the damage occurs [25, 26]. Thus, the coating has shown good self-healing properties and able to protect the substrate. Suryanarayana *et al.* [17] indicated that the effective self-healing coating, when the microcapsules incorporated in the paint film, break immediately to release healing material when the cracks are generated in the paint film. It is also observed that the shell surface of microcapsules is very rough which will provide good bonding with the film matrix [17].

3.2 Immersion Test

In order to investigate the corrosion behaviour of the self-healing microcapsule embedded in epoxy coated samples, the immersion test was conducted from one to eight weeks. The corrosion product appeared to form on the pure epoxy coated sample. This indicates that chloride ions was able to penetrate through the plain epoxy coating which results in corrosion taking place on the steel substrate material. However there is hardly any corrosion product observed on the self-healing coated sample after seven days of immersion due to excellent performance of healing agent to heal the damaged region.

Based on the visual observation results shown in Table 2, the corrosion products were mostly found on the pure epoxy coated samples. From Table 2, no delamination, blisters, peeling and cracking defects observed on both coated samples [30, 31]. While there was less corrosion product visible on the surface of zeolite microcapsule embedded in epoxy self-healing coated sample. This is again due to the less protective behaviour shown by the pure epoxy coating compared to the self-healing coating. Based on visual inspection after four weeks and six weeks immersion in 3.5% NaCl medium, it was found that the amount of corrosion product increased on the surface of pure epoxy coated samples compared to self-healing coated samples. However the amount of corrosion product was observed on the self-healing coating indicating that some areas were not fully protected with the healing agent.

As expected, the amount of corrosion product was mostly found on samples coated with pure epoxy after eight weeks immersion compared with the self-healing coated samples. Corrosion product was also formed on the self-healing coated samples because chloride ions was able to break the unprotected area of coating after prolong exposure and the microcapsules were not able to heal all the coating surfaces. The overall weight loss measurements of immersion test and corrosion rates are plotted in Figures 3 and 4. Similar to previous studies which concluded that the outstanding anticorrosion function of self-healing coating towards steel substrates was attributed to the fact that the released healing agent from ruptured microcapsules can seal and heal

automatically the damaged area [25, 27-31]. However, the empty crack within control specimens results in the direct exposure of steel substrates to surrounding corrosive solutions [27].

Table 2 Visual inspection of pure epoxy and self-healing coated samples after 1, 2, 4, 6 and 8 weeks of immersion test in 3.5% NaCl medium

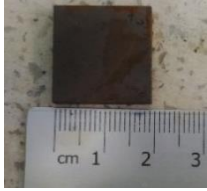
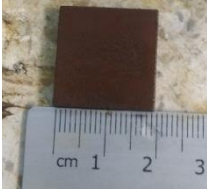
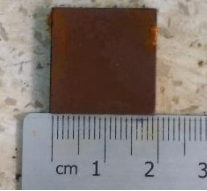
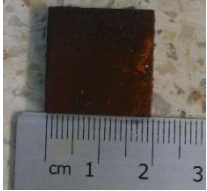
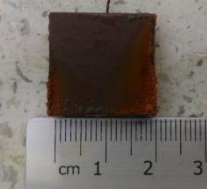
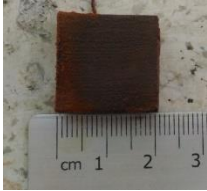
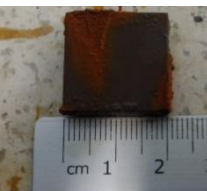



Immersion times	Pure Epoxy Paint	Self-Healing Coating
1 Week (7 days)		
2 weeks (14 days)		
4 weeks (48 days)		
6 weeks (42 days)		
8 weeks (56 days)		

Figure 3 shows that the weight loss for the pure epoxy coated samples increases as immersion time increases. On the other hand, the self-healing coated samples increases initially but it starts to decrease after four weeks of immersion test. This is because the self-healing coated samples began to repair or heal the damage coating by releasing the zeolite microcapsule which then protected the sample from further corrosion. Even though amount of weight loss decreases, the corrosion product was still observed on the samples after prolong exposure because not all the microcapsules would be released from the coating.

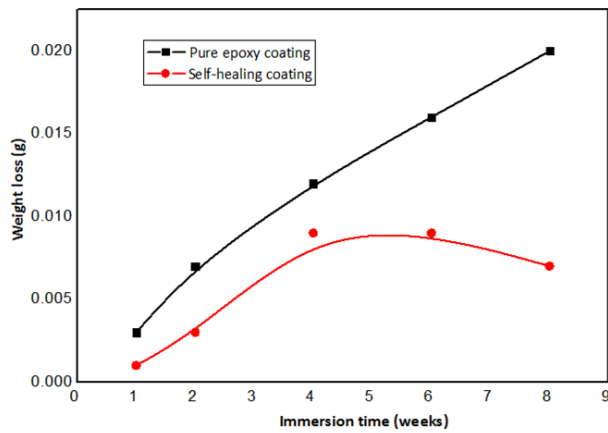


Figure 3 Weight loss against immersion period for pure epoxy and self-healing coated samples after immersed in 3.5% NaCl medium

Figure 4 presents the corrosion rate generally decreases. It can be explained that after some time the chloride ions from the 3.5% NaCl medium would be depleted. Hence it will slow down the corrosion process. Furthermore, the formation of corrosion products on the surface of the samples also provided a barrier against corrosion. The pure epoxy coated samples has higher corrosion rate compare to the self-healing coated samples because the epoxy coating had been attacked by the corrosive solution was not recovered and this would make the samples to undergo corrosion. Meanwhile for self-healing coated samples which were covered by a layer of zeolite microcapsules that were embedded in the epoxy coating especially at scribed region was able to slow down the corrosion process. The zeolite was released from the microcapsule when the coating was ruptured during the corrosion attack.

When the coating was repaired or healed again it would protect the underlying steel substrate sample from further corrosion. Hence this justifies why the corrosion rate of self-healing coated samples is lower than pure epoxy coated samples.

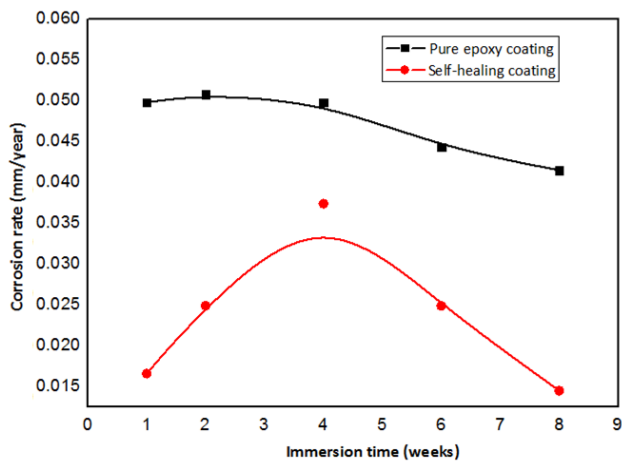


Figure 4 Corrosion rate against immersion period for pure epoxy and self-healing coated samples after immersed in 3.5% NaCl medium

3.3 Salt Spray Test

A salt spray test was conducted on a different batch of samples with the same area size of 20 x 20mm with 3.5% NaCl medium for fourteen days exposure times. The samples were taken out from the salt spray chamber at an interval 3, 7, 10 and 14 days. Based on visual inspection as shown in Table 3, no blisters, peeling and cracking observed on both coated samples, while present of corrosion product on scribed area and uncoated sample was observed. The uncoated samples suffer severe corrosion due to aggressive environment in the salt fog chamber. Large amount of corrosion product was found on the surface samples. Even after cleaning the uncoated sample, the black residue was still found on the sample. Corrosion product was also observed at the scratch made on pure epoxy coated sample. However less corrosion product could be seen on self-healing coated samples.

After 10 days of salt spray test, uncoated and pure epoxy coated samples were found to produce excessive amount of corrosion product, but the most severe was the uncoated sample. For the self-healing coating, less corrosion product was formed on the surface. After 14 days of exposure, similar outcomes were observed on all coated and uncoated samples. The uncoated samples exhibit the maximum amount of corrosion product compare to pure epoxy coated and self-healing coated samples. The scratch on the self-healing coated samples was seen to be covered with polymer material compare to the pure epoxy coated and uncoated samples. This probably due to the scratches initiated the zeolite from the microcapsule to form a new layer of protective film and function as a self-healing coating. Previous studies also reported similar findings whereby self-healing coating provides better corrosion resistant than original coating after exposed to very aggressive environment condition [32-35]. All the self-healing coated samples remain intact with absent or little rust, no peeling and blisters after exposure to salt environment while the original coated sample at scribed areas are full of rust and blisters [34].

Table 3 Visual inspection of uncoated, pure epoxy and self-healing coated samples after 3, 7 10 and 14 days of salt spray test

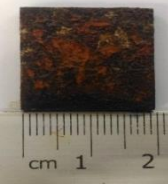


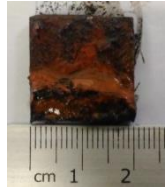

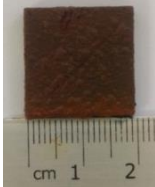
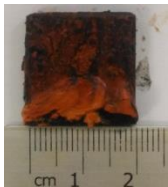




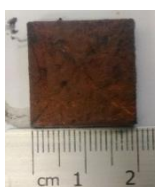
Exposure times (day)	Sample		
	Uncoated sample	Pure Epoxy coating	Self-healing coating
3 Days			
7 Days			
10 Days			
14 Days			

Figure 5 shows the weight loss for each type of samples increases with exposure times. This indicates that the corrosion activity contributes to the weight loss of the sample. It shows that uncoated sample has suffered the highest increase of weight loss followed by pure epoxy coated sample. The self-healing coated sample gives the lowest weight loss. The excellent protection of self-healing coated samples began to repair or heal the damage coating by releasing the zeolite microcapsules which then formed a new layer of protective film to the sample and prevented the samples from further corrosion.

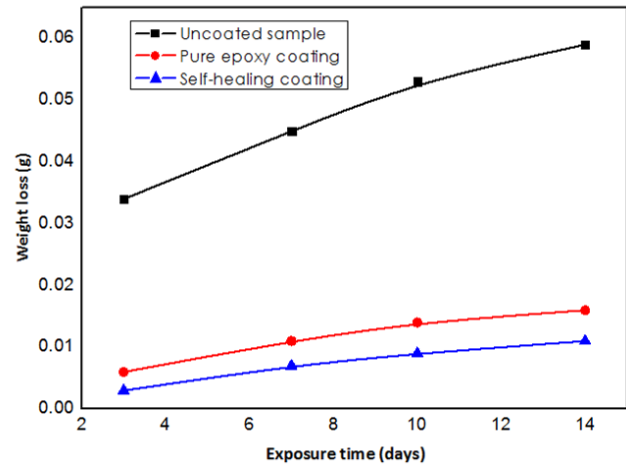


Figure 5 Weight loss against exposure times for uncoated, pure epoxy and self-healing coated samples after salt spray test

Corrosion rates for all samples after salt spray test are shown in Figure 6. The results generally show decreasing trend of corrosion rate. The highest corrosion rate was observed on the uncoated sample followed by pure epoxy coated and finally self-healing coating. The uncoated samples suffered most of the corrosion because there is no protective film on the samples to prevent the corrosion. On the other hand the reason pure epoxy coated samples show higher corrosion rate compared to the self-healing coated sample because once the coating was damaged, no further protection was provided on steel substrates. The scribed region on the self-healing coating surface triggered the zeolite microcapsule to rupture and release the functionalized zeolite to form the new protective layer while the scratch of pure epoxy coated are left bare. This new protective layer would prevent the contact of the surface samples to the corrosive environment thus prevent further corrosion to occur on the samples. All samples show decreasing corrosion rate due to corrosion product formed on the surface and hence reduced the contact between solution and the metal surface.

Based on Figure 7 we can see that the self-healing abilities of the zeolite microcapsules became significant after seven days of exposure. Observation after 14 days shows that the zeolite microcapsules were able to completely cover the scratch region on the substrate material, hence it would prevent further corrosion. The scratch area was sealed to retard the diffusion of corrosive salt solution and thus protect the substrate from corrosion [28].

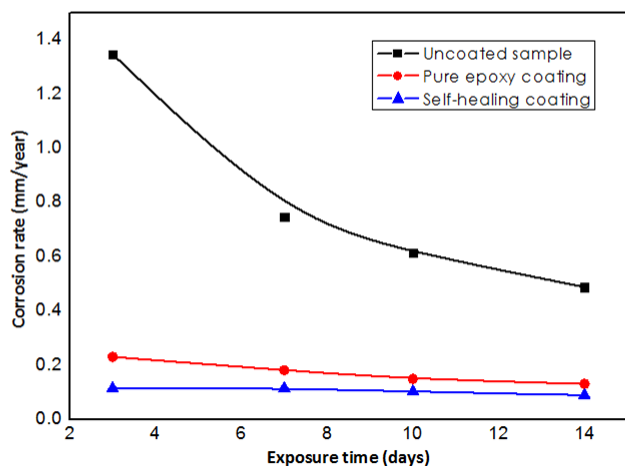


Figure 6 Corrosion rate against exposure times for uncoated, pure epoxy and self-healing coated samples after salt spray test

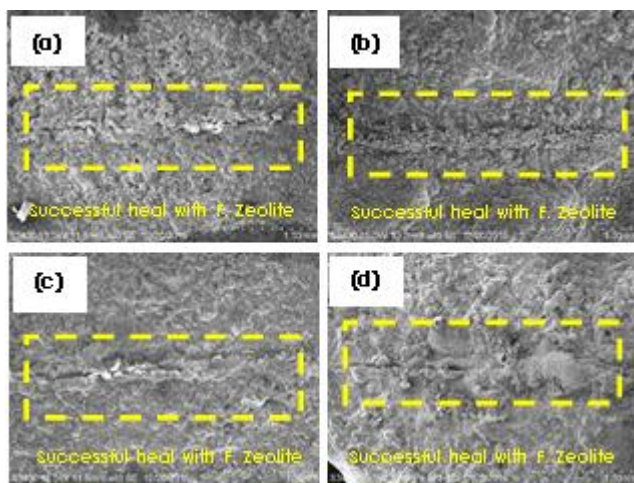


Figure 7 VPSEM image of scribed region on self-healing coated samples after salt spray test for (a) 3 (b) 7 (c) 10 and (d) 14 exposure days

4.0 CONCLUSIONS

In this study, the PUF microcapsules containing functionalized zeolite were successfully synthesized via in-situ polymerization method. This study has shown potential for developing self-healing anticorrosion coating by incorporating with 20wt. % microcapsules concentration into epoxy paints. A successful release of the zeolite from the capsules embedded in the epoxy coating upon mechanical damage was confirmed by VPSEM image.

From the immersion and salt spray test of anticorrosion performance of self-healing coating, the microcapsules ruptured and released the zeolite material, which healed cracks efficiently with satisfactory anticorrosive properties during mechanical damaged. Thus, this coating significantly enhanced the anti-corrosion performance and decreased the

corrosion rate of the coated low carbon steel substrates. The self-healing coating has good ability to repair the damage that occur on the coating of a steel substrate by releasing the healing agent in the microcapsules embedded in the epoxy matrix and sealed the exposed area from further corrosion.

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References

- [1] Szczepanowicz, K., Mordarski, G., Podgórna, K., Socha, R., Nowak P., Warsynski P., and Hack T. 2015. Self-healing Epoxy Coatings Loaded with Inhibitor-containing Polyelectrolyte Nanocapsules. *Prog. in Org. Coatings*. 84: 97-106.
- [2] Kumar, A., Stephenson, L. D., and Murray, J. N. 2006. Self-Healing Coatings for Steel. *Prog. in Org. Coatings*. 55: 244-253.
- [3] Siva, T., Sathiyarayanan, S. 2015. Self-healing Coatings Containing Dual Active Agent Loaded Urea Formaldehyde (UF) Microcapsules. *Prog. in Org. Coatings*. 82: 57-67.
- [4] Yu, D., Zhi, M. and Qiu, M., 2015, Self-healing Polymeric Materials Based on Microencapsulated Healing Agents: From Design to Preparation. *Prog. in Polym. Sci.* 49-50: 175-220.
- [5] Lang, S. and Zhou, Q. 2017. Synthesis and Characterization of Poly(Urea-Formaldehyde) Microcapsules Containing Linseed Oil for Self-healing Coating Development. *Prog. in Org. Coatings*. 105: 99-110.
- [6] Leping, L., Wei, Z., Yi, X. I. N., Hongmei, W., Yang Z. and Wu J. L. 2011. Preparation and Characterization of Microcapsule Containing Epoxy Resin and Its Self-healing Performance of Anticorrosion Covering Material. *Chinese Science Bulletin*. 56: 439-443.
- [7] Blaiszik, B. J., Caruso, M. M., McIlroy, D. A., Moore, J. S., White S. R., and Sottos, N. R. 2009. Microcapsules Filled with Reactive Solutions for Self-healing Materials. *Polymer*. 50: 990-997.
- [8] Bollinger, J., Britton, J., Gisin, N., Knight, P., Brown E. N. and Viswanathan, S. 2001, Autonomic Healing of Polymer Composites. *Letters to Nature*. 409: 1804-1807.
- [9] García, S. J., Fischer, H. R., Zwaag and S. Van Der. 2011. A Critical Appraisal of the Potential of Self-healing Polymeric Coatings. *Prog. in Org. Coatings*. 72: 211-221.
- [10] Samadzadeh, M., Boura, S. H., Peikari, M., Kasriha and S. M., Ashrafi, A. 2010. A Review on Self-Healing Coatings Based on Micro/Nanocapsules. *Prog. in Org. Coatings*. 68: 159-164.
- [11] Gonzalez, S. and Kittel, J. 2008. Self-healing Coatings: An Alternative Route for Anticorrosion Protection. *Prog. in Org. Coatings*. 63: 307-315.
- [12] Nesterova, T., Dam-johansen, K. and Kil, S. 2011. Synthesis of Durable Microcapsules for Self-healing Anticorrosive Coatings: A Comparison Of Selected Methods. *Prog. in Org. Coatings*. 70: 342-352.
- [13] Nesterova, T., Dam-johansen, K., Thorslund, L. and Kil, S. 2012. Microcapsule-based Self-healing Anticorrosive Coatings: Capsule Size, Coating Formulation, and Exposure Testing. *Prog. in Org. Coatings*. 75: 309-318.
- [14] Islam, N., Halder, S. and Goyat, M. S. 2016. Effect of Epoxy Resin and Hardener Containing Microcapsules on Healing

- Efficiency of Epoxy Adhesive Based Metal Joints. *Mater. Chem. Phys.* 171: 267-275.
- [15] Paliwoda-porebska, G., Stratmann, M. and Rohwerder, M. 2005. On the Development of Polypyrrole Coatings with Self-healing Properties for Iron Corrosion Protection. *Corrosion Science*. 47: 3216-3233.
- [16] Yang, Z., Wei, Z., Le-Ping W., Mei, W. H., and Jun, L. W. 2011. The Self-healing Composite Anticorrosion Coating. *Physics Procedia*. 18: 216-221.
- [17] Suryanarayana, C., Rao, K.C. and Kumar, D. 2008. Preparation and Characterization of Microcapsules Containing Linseed Oil and Its Use in Self-healing Coatings. *Prog. in Org. Coatings*. 63: 72-78.
- [18] Boura, S. H., Peikari, M., Ashrafi, A. and Samadzadeh, M. 2012. Self-healing Ability and Adhesion Strength of Capsule Embedded Coatings-Micro and Nano Sized Capsules Containing Linseed Oil. *Prog. in Org. Coatings*. 75: 292-300.
- [19] Aishah, S., Hanim, M., Ahmad, N., Nik and N., Ibrahim, Z., 2017. Analyses of surface Area, Porosity, Silver Release and Antibacterial Activity of Amine-functionalized, Silver-Exchanged Zeolite NaY. *Vaccum*. 143: 344-347.
- [20] Sánchez, M. J., Mauricio, J. E., Paredes, A. R., Gamero and P., Cortés, D. 2017. Antimicrobial Properties of ZSM-5 Type Zeolite Functionalized with Silver. *Material letters*. 191: 65-68.
- [21] ASTM G31-24. 2004. Standard Practice for Laboratory Immersion Corrosion Testing of Metals. ASTM International, West Conshohocken, PA.
- [22] ASTM B117-11. Standard Practice for Operating Salt Spray (Fog) Apparatus. ASTM International, West Conshohocken, PA.
- [23] Liu, X., Zhang, H., Wang, J., Wang, Z. and Wang, S. 2012. Preparation of Epoxy Microcapsule Based Self-healing Coatings And Their Behavior. *Surf. & Coat. Technol.* 206: 4976-4980.
- [24] Yang, Z., Wei, Z., Le-ping, L., Si-jie, W. and Wu-jun, L., 2012. Self-healing Coatings Containing Microcapsule. *Appl. Surf. Sci.* 258: 1915-1918.
- [25] Thanawala, K., Mutneja, N., Khanna, A. S. and Raman, R. K. S. 2014. Development of Self-healing Coatings based on Linseed Oil as Autonomous Repairing Agent for Corrosion Resistance. *Materials*. 7: 7324-7338.
- [26] Manasa, S., Jyothirmayi, A., Siva, T., Sathiyarayanan, S., Gobi, K. V. and Subasri R. 2017. Effect of Inhibitor Loading into Nanocontainer Additives of Self-healing Corrosion Protection Coatings on Aluminum Alloy A356. *J. Alloys Compd.* 726: 969-977.
- [27] Sun, D., Zhang, H., Tang, X. and Yang, J. 2016. Water Resistant Reactive Microcapsules for Self-healing Coatings in Harsh Environments. *Polymer*. 91: 33-40.
- [28] Huang, M., Zhang, H. and Yang, J. 2012. Synthesis of Organic Silane Microcapsules for Self-healing Corrosion Resistant Polymer Coatings. *Corros. Sci.* 65: 561-566.
- [29] Kouhi, M., Mohebbi, A., Mirzaei, M. and Peikari, M. 2013. Optimization of Smart Self-healing Coatings Based on Micro/Nanocapsules in Heavy Metals Emission Inhibition. *Prog. in Org. Coatings*.
- [30] Plawecka, M., Snihirova, D., Martins, B., Szczepanowicz, K., Warszynski, P. and Montemor, M. F. 2014. Self Healing Ability of Inhibitor-containing Nanocapsules Loaded in Epoxy Coatings Applied on Aluminium 5083 and Galvanneal Substrates. *Electrochimica Acta*. 140: 282-293.
- [31] Salehi, E., Naderi, R. and Ramezanzadeh, B. 2017. Improvement in the Protective Performance of Epoxy Ester Coating Through Inclusion of an Effective Hybrid Green Corrosion Inhibitive Pigment. *J. Taiwan Inst. Chem. Eng.* 000: 1-15.
- [32] Kongparakul, S., Kornprasert, S., Suriya, P. and Le, D. 2017. Self-healing Hybrid Nanocomposite Anticorrosive Coating From Epoxy/Modified Nanosilica/Perfluorooctyl Triethoxysilane. *Prog. in Org. Coatings*. 104: 173-179.
- [33] Huang, M. and Yang, J. 2014. Salt Spray and EIS Studies on HDI Microcapsule-based Self-healing Anticorrosive Coatings. *Prog. in Org. Coatings*. 77: 168-175.
- [34] Hao, Y., Liu, F. and Han, E., 2013. Protection of Epoxy Coatings Containing Polyaniline Modified Ultra-short Glass Fibers. *Prog. in Org. Coatings*. 76: 571-580.
- [35] Jadhav, A. J., Holkar, C. R. and Pinjari, D. V. 2018. Anticorrosive Performance of Super-hydrophobic Imidazole Encapsulated Hollow Zinc Phosphate Nanoparticles on Mild Steel. *Prog. in Org. Coatings*. 114: 33-39.