

Characterization of Encapsulated Corrosion Inhibitors for Environmentally Friendly Smart Coatings

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Summary

The NASA Kennedy Space Center's Corrosion Technology Lab at the Kennedy Space Center in Florida, U.S.A. has been developing multifunctional smart coatings based on the microencapsulation of environmentally friendly corrosion indicators, inhibitors and self-healing agents. This allows the incorporation of autonomous corrosion control functionalities, such as corrosion detection and inhibition as well as the self-healing of mechanical damage, into coatings. This paper presents technical details on the characterization of inhibitor-containing particles and their corrosion inhibitive effects using electrochemical and mass loss methods.

Three organic environmentally friendly corrosion inhibitors were encapsulated in organic microparticles that are compatible with desired coatings. The release of the inhibitors from the microparticles in basic solution was studied. Fast release, for immediate corrosion protection, as well as long-term release for continued protection, was observed.

The inhibition efficacy of the inhibitors, incorporated directly and in microparticles, on carbon steel was evaluated. Polarization curves and mass loss measurements showed that, in the case of 2-MBT, its corrosion inhibition effectiveness was greater when it was delivered from microparticles.

1. Introduction

The corrosion of metals is a problem with great economic and social impact. It was estimated to have cost the world economy over \$2 trillion dollars in 2010 [1] and the loss of the structural integrity of buildings, bridges, automobiles, airplanes, etc. poses a significant safety issue to society.

One approach to preventing corrosion is the use of inhibitors within coatings [2]. In recent years, the use of some highly effective corrosion inhibitors, such as chromates, has been banned or are in the process of being phased out, due to their carcinogenicity [3]. In the quest to find suitable replacements, as well as the general trend towards using "green" technologies", environmentally friendly alternatives are being investigated [4]. Some promising materials, however, due to low or high solubility or coating incompatibility cannot be used as drop-in replacements.

In an effort to overcome the limitations of these promising candidates, multiple approaches to the development of delivery systems for these materials have been taken [3] [6]. This has involved the encapsulation into nano- and microparticles and -capsules [2] [3] [9] [10], the absorption into meso- and macroporous synthesized or naturally occurring materials [11] [5] [6] [7] [15], as well as the incorporation into double-layer hydroxides [9] and layer-by-layer polymer structures [7] [8] [19].

The NASA Kennedy Space Center's Corrosion Technology Lab has been developing multifunctional smart coatings based on the microencapsulation of environmentally friendly corrosion indicators, inhibitors and self-healing agents for several years. This paper focuses on the evaluation of three different compounds, both in their pure form and encapsulated in microparticles, as corrosion inhibitors for carbon steel using electrochemical methods and mass loss experiments.

2. Experimental Procedure

2.1. Encapsulation procedure

Three different inhibitors, phenylphosphonic acid (PPA), 8-hydroxyquinoline (8-HQ) and 2-mercaptobenzothiazole (2-MBT) were encapsulated into pH-sensitive organic microparticles using emulsion polymerization [20].

2.2. Total Inhibitor Content and Release Studies

The total inhibitor content of 2-MBT particles was determined using elemental analysis. Approximately 5 mg of particles in tin samples vessels were placed in a Vario EL III CHNS Elemental Analyzer instrument. The samples were combusted in oxygen with helium as the carrier gas. The carbon, hydrogen, nitrogen and sulfur content was determined by a thermal conductivity detector. Sulfanilic acid was used to calibrate the instrument.

The release of 2-MBT from microparticles was determined. Microparticles were dispersed in 20 ml 0.01 M KOH at a concentration of 1000 mg/g and continually stirred at 300 rpm. Aliquots of samples were taken after 1 h, 24 h, 1 week, 2 weeks, 4 weeks and every following 4 weeks until no further release was observed. Samples were filtered through a 0.2 μm nylon filter and appropriately diluted with acetonitrile. The concentration of the inhibitors was measured using a Thermo Fisher Scientific Accela HPLC with a Varian Polaris C18-A column and a diode array detector. A gradient run was performed at 200 $\mu\text{l}/\text{min}$ with 0.1% phosphoric acid in water and acetonitrile as the mobile phase. The concentrations of the inhibitors were determined at a wavelength of 320 nm.

2.3. Polarization curves

One inch (2.54 cm) diameter 1018 carbon steel coupons were embedded in an epoxy stub with an attached, insulated copper connection. The samples were immersed in 200 ml of 3.5% NaCl solution/suspensions containing inhibitors, added directly or in microparticles, at the concentrations shown in Table 1. To maximize dissolution, the pure inhibitor solutions were heated to 90 $^{\circ}\text{C}$ and cooled to room temperature. The pH of the solutions were adjusted to 5.5 using either HCl or NaOH. A silver/silver chloride (SSC) electrode was used as the reference and a graphite rod as the counter electrode. The samples were left in solution for 17 hours to allow them to reach a steady state open circuit potential (OCP), before beginning polarization measurements. Anodic and cathodic polarization curves were obtained for freshly polished samples each time. The coupons were polarized from 30 mV below OCP to 1.5 V (for anodic scans) and 30 mV above OCP to -1.5 V (for cathodic scans). Triplicate samples were run for each condition.

2.4. Mass Loss Testing

3 in (7.62 cm) x 1 in (2.54 cm) x 0.06 in (0.15 cm) 1018 carbon steel panels were cleaned using 0.025 M hexamethylene tetramine in 18.5% HCl (based on ASTM G1-90 and G3-03) and weighed to 0.1 mg. The panels were immersed in 200 ml of 3.5% NaCl solution/suspensions containing inhibitors or microparticles at the concentrations outlined in Table 1. To maximize dissolution, the pure inhibitor solutions were heated to 90 $^{\circ}\text{C}$ and cooled to room temperature. The pH of the solutions was adjusted to pH 5.5 using either HCl or NaOH. Triplicate samples were removed from solution after 3 days, 10 days and 28 days. The panels were photographed, cleaned using the same procedure described above, and weighed to 0.1 mg.

Table 1: Concentrations in wt% of inhibitors and particles in 3.5% NaCl suspensions

	PPA	8-HQ	2-MBT
Inhibitors	0.1	0.1	0.1
Particles	0.3	0.25	0.2

3. Results & Discussion

3.1. Encapsulation

For this work, PPA, 8-HQ and 2-MBT encapsulated in polymeric microparticles were used based on the synthesis process described in the referenced patent [20]. **Figure 1** shows SEM images of various microparticle formulations and a photo showing the microparticles as free-flowing powders. This allows for simple, safe handling and incorporation into existing coatings systems.

In this paper, when referring to solutions containing an inhibitor or particle, it will be labeled as the name of the inhibitor followed by Inh for the pure inhibitor and Part for the particles, e.g. 8-HQ Inh or 2-MBT Part.

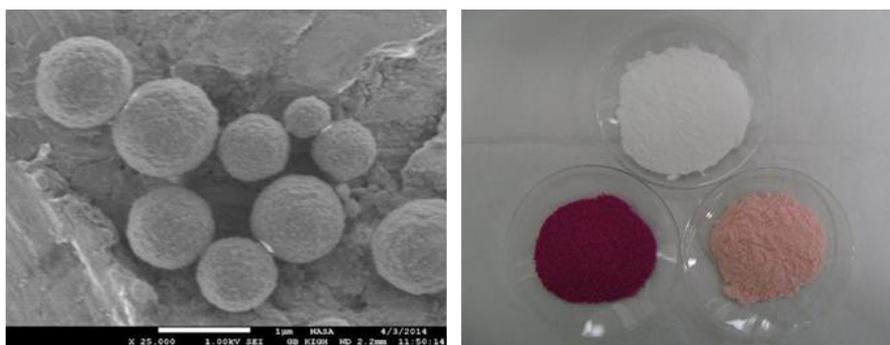


Figure 1: Images of microparticles in SEM (left) and as free-flowing powders (right)

3.2. Inhibitor Content and Release Behavior

The total inhibitor content of the 2-MBT Part was determined. Particles with inhibitor concentrations ranging from 16 to 60 wt% were synthesized. The cumulative release of 2-MBT from three generations of organic particles in 0.01 M KOH is shown **Figure 2**.

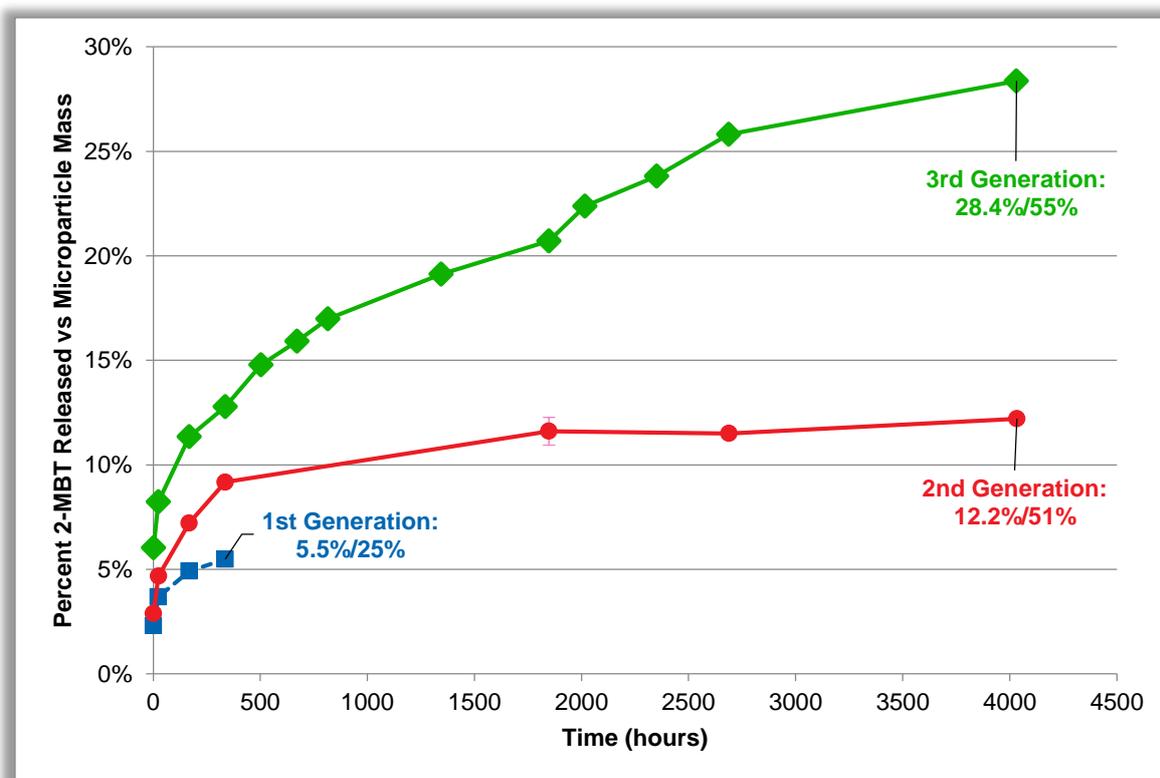


Figure 2: Cumulative release of inhibitor from organic 2-MBT particles

The 2-MBT particles have a low initial release (<6% after 1 hour), followed by a slow but consistent release over time. In successive iterations of the microparticle formulae, it was possible to not only double the inhibitor payload but also to significantly increase the amount of released material and the period of time over which it is released. The third generation of these microparticles, which were used for all testing, where the inhibitor content was consistently found to be 55 ± 2 wt%, released half of their payload after exposure to base solution for 18 weeks.

3.3. Accelerated Corrosion Testing: PPA

The polarization curves of PPA Inh, PPA Part and the Control sample are plotted in Figure 3. Neither PPA Inh nor PPA Part show significant changes in the corrosion potential or anodic polarization, which are indicative of corrosion inhibition. A slight shift in the cathodic polarization curve between 10^{-5} and 10^{-4} A/cm² suggests that the inhibitor is affecting certain cathodic reactions. The precise origin of this effect could be determined by further electrochemical measurements, e.g. by excluding oxygen.

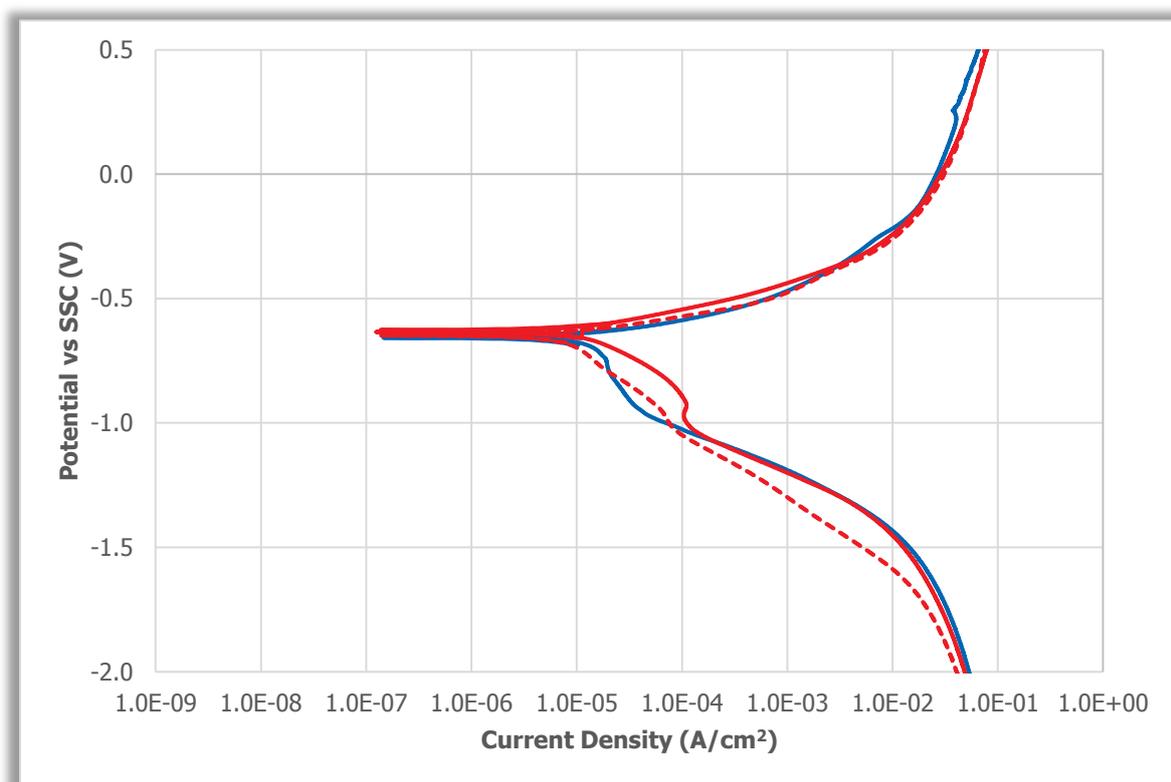


Figure 3: Polarization curves of carbon steel in the presence of PPA inhibitor (solid red), PPA particle (dashed red) and the Control (solid blue)

Similar behavior is observed in the mass loss experimental results. **Figure 4** shows the corrosion rate (CR) in terms of carbon steel mass loss (mg/cm²) of PPA Inh and PPA Part measured during the mass loss experiments. The pure inhibitor and particles exhibit the same or even higher mass loss than the control sample. This is despite the fact that this inhibitor exhibited some of the best corrosion protection behavior, based on the appearance of the corrosion test panels. **Figure 5** shows the Control and PPA Inh panels after they were removed from solution and cleaned with water after 10 days of immersion. A gray film of PPA adhered to the surface gives the impression of a well-protected metal (a similar film is observed for PPA Part after 3 days). Though PPA bonds well with iron, it is most effective when used as pretreatment [20], especially in combination with other protective agents [21] [22] [23]. In the conditions where exposure to PPA and corrosion are occurring at the same time, despite its appearance, the PPA film on the metal does not significantly protect the panels.

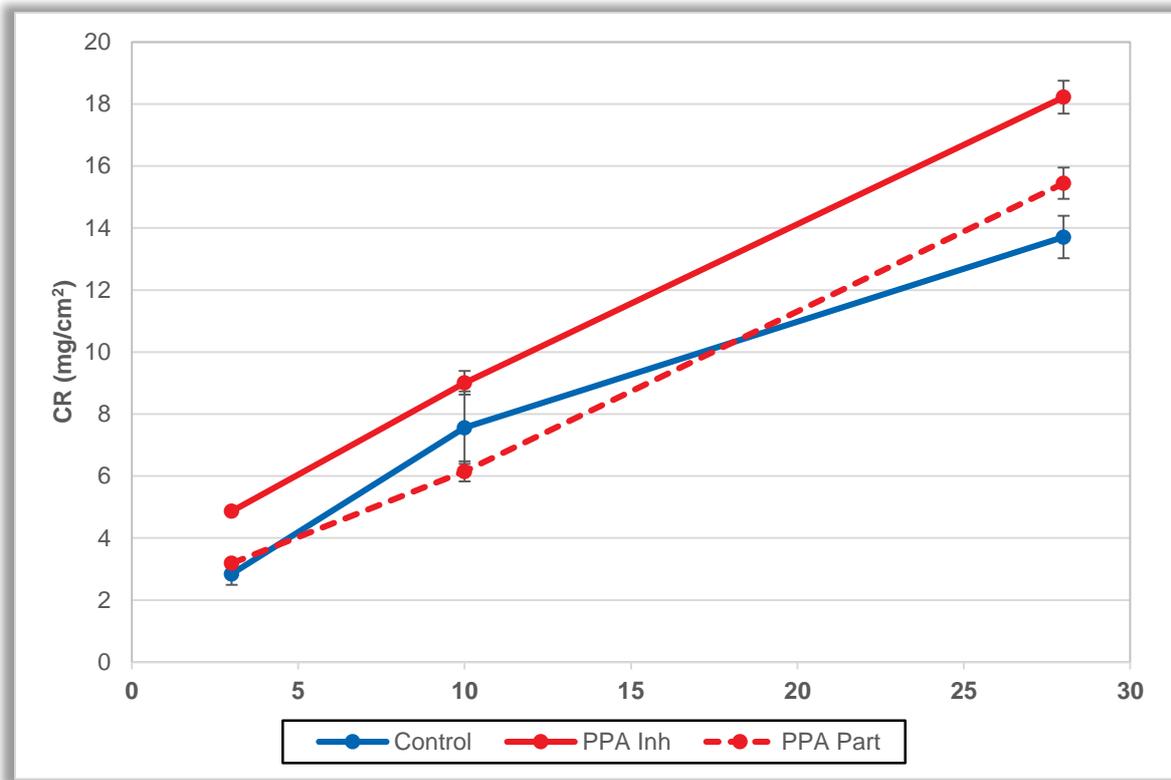


Figure 4: Corrosion rate of carbon steel in the presence of PPA Inh, PPA Part and Control as a function of immersion time

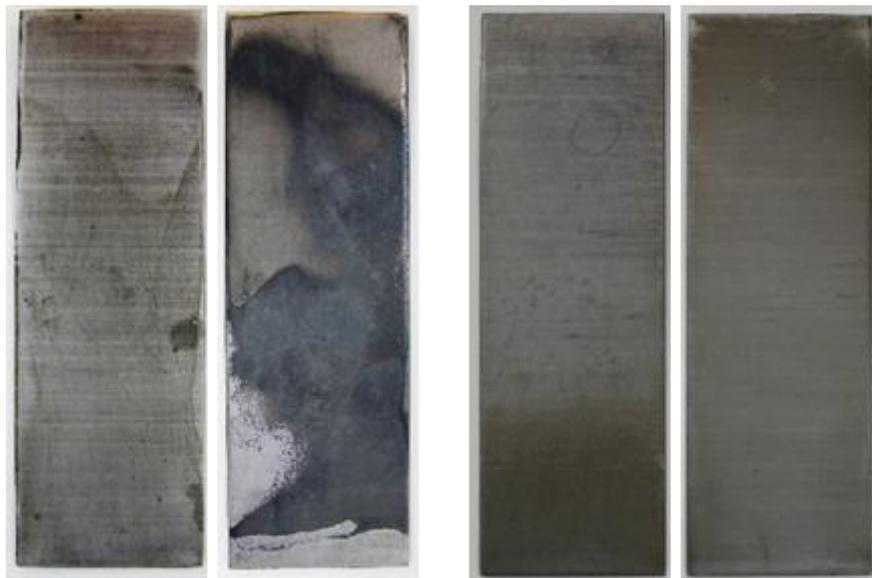


Figure 5: Front and back of Steel panels after immersion in 3.5% NaCl for 10 days Left: Front and back of Control; Right: Front and back of PPA inhibitor

3.4. Accelerated Corrosion Testing: 8-HQ

The polarization curves of 8-HQ Inh, 8-HQ Part and the Control sample are plotted in **Figure 6**. The presence of 8-HQ Inh causes a shift in the corrosion potential to more positive (passive) potential values, and a decrease in the corrosion current density. This data shows that 8-HQ inhibits both the anodic and cathodic corrosion reactions. Similar behavior has been observed for 8-HQ on other metals in different electrolytes, and the inhibition is attributed to the complexation with metal ions, absorption onto the metal surface, and film formation [20] [21] [22]. The same behaviors were not observed for the 8-HQ particles, where no notable inhibition is apparent. This data suggests that the

release properties of the particles are not adequate to provide corrosion protection within the test conditions.

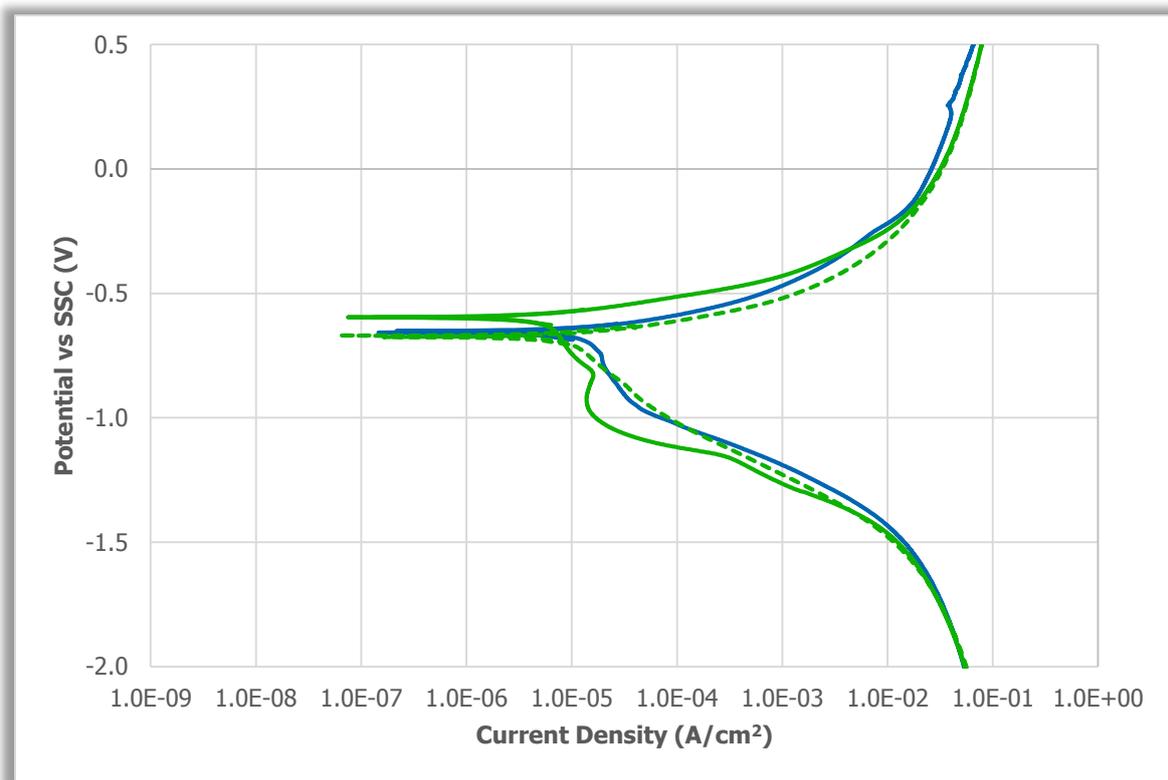


Figure 6: Polarization curves of carbon steel in the presence of 8-HQ inhibitor (solid green), particle (dashed) and the Control (solid blue)

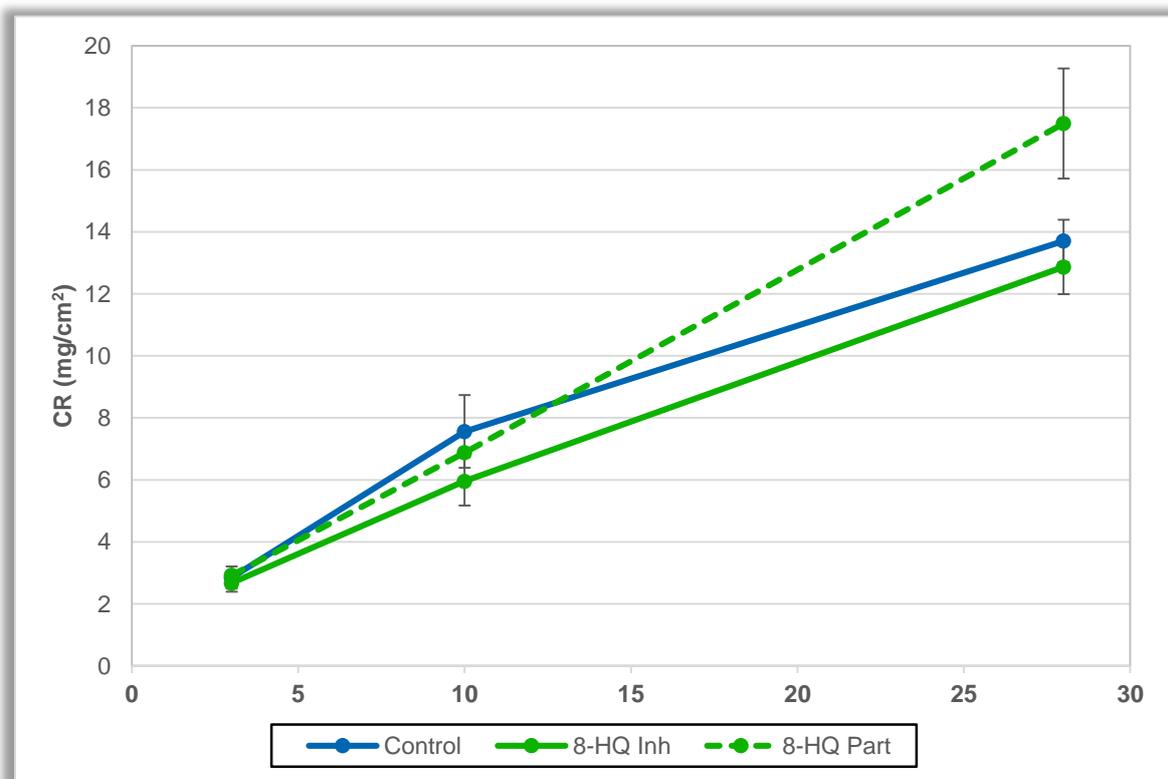


Figure 7: Corrosion rate of carbon steel in the presence of 8-HQ Inh, 8-HQ Part and Control as a function of immersion time

The corrosion inhibition identified in the electrochemical measurements for 8-HQ Inh is not observed in the mass loss test results. These results, for both the inhibitor and the particles, show no significant corrosion inhibition when compared to the control. The inhibitor-filled particles appeared to even perform worse than the control after 28 days of immersion. Within the test conditions, exposing a very reactive metal, carbon steel, to a very corrosive solution, 3.5% NaCl, 8-HQ is unable to provide corrosion protection over longer periods of time. The rate of corrosion of the carbon steel in the aggressive NaCl solution is likely too high for the 8-HQ inhibitor to make any notable impact in inhibiting the metal over longer periods of time.

3.5. Accelerated Corrosion Testing: 2-MBT

The polarization curves of carbon steel in the presence of 2-MBT inhibitor, 2-MBT particles, and the Control sample are plotted in **Figure 8**. The presence of 2-MBT provides significant protection to the metal, acting as a mixed type inhibitor by absorbing onto the metal surface and slowing both the anodic and cathodic reactions [29] [30] [31]. The corrosion potential is shifted over 130 mV vs SCC to more positive potentials accompanied by a decrease in the corrosion current by nearly one order of magnitude. The 2-MBT particles exhibit the same behavior as the pure inhibitor, demonstrating that the particles are delivering a sufficient amount of 2-MBT to the metal to inhibit corrosion.

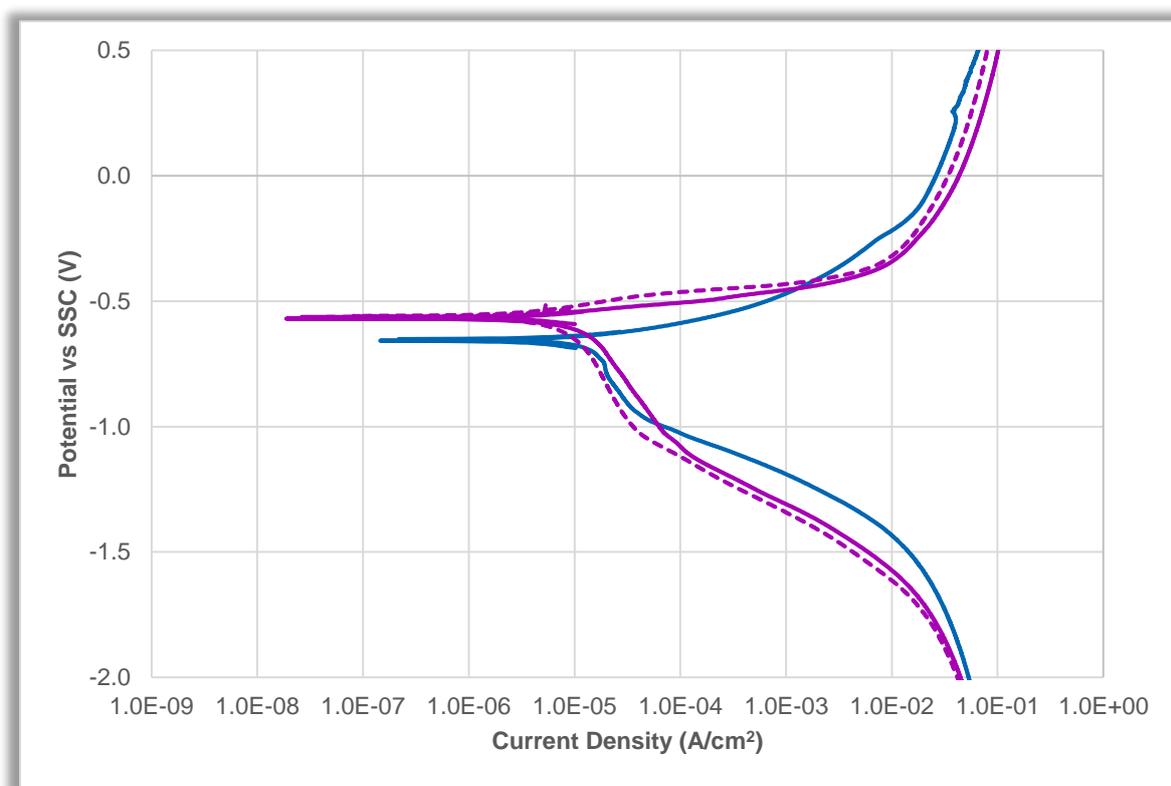


Figure 8: Polarization curves of carbon steel in the presence of 2-MBT inhibitor (solid purple), 2-MBT particle (dashed purple) and the Control (solid blue)

The mass loss test method showed that the 2-MBT inhibitor exhibits the same or even a worse corrosion rate than the Control. In contrast, the 2-MBT particles perform significantly better than the Control over the whole range of 28 days of immersion.

There are a couple of reasons for the higher performance of the 2-MBT particle over the pure inhibitor. For one, 2-MBT is nearly insoluble in neutral and acidic media. Consequently, as opposed to the 2-MBT inhibitor which only has low amounts of inhibitor dissolved in solution, the 2-MBT particles can, as designed, deliver the inhibitor directly to active corrosion sites, where the pH is elevated, resulting in the targeted release of 2-MBT into the reactive area. Secondly, as discussed earlier (see **Figure 2**), 2-MBT particles are able to quickly release small, but significant amounts of their payload to inhibit

corrosion and then continue to release inhibitor over long periods of time, providing immediate as well as continuous long term corrosion protection.

The contrast between the electrochemical measurements and the mass loss experiments for the pure inhibitor is thought to be due to the longer immersion times used in the mass loss experiments. Polarization curves are measured after 17 h, whereas the first mass loss data was obtained after 3 days (72 h). During this time, the pure inhibitor ceases to be effective, whereas the 2-MBT particle can provide continued protection.

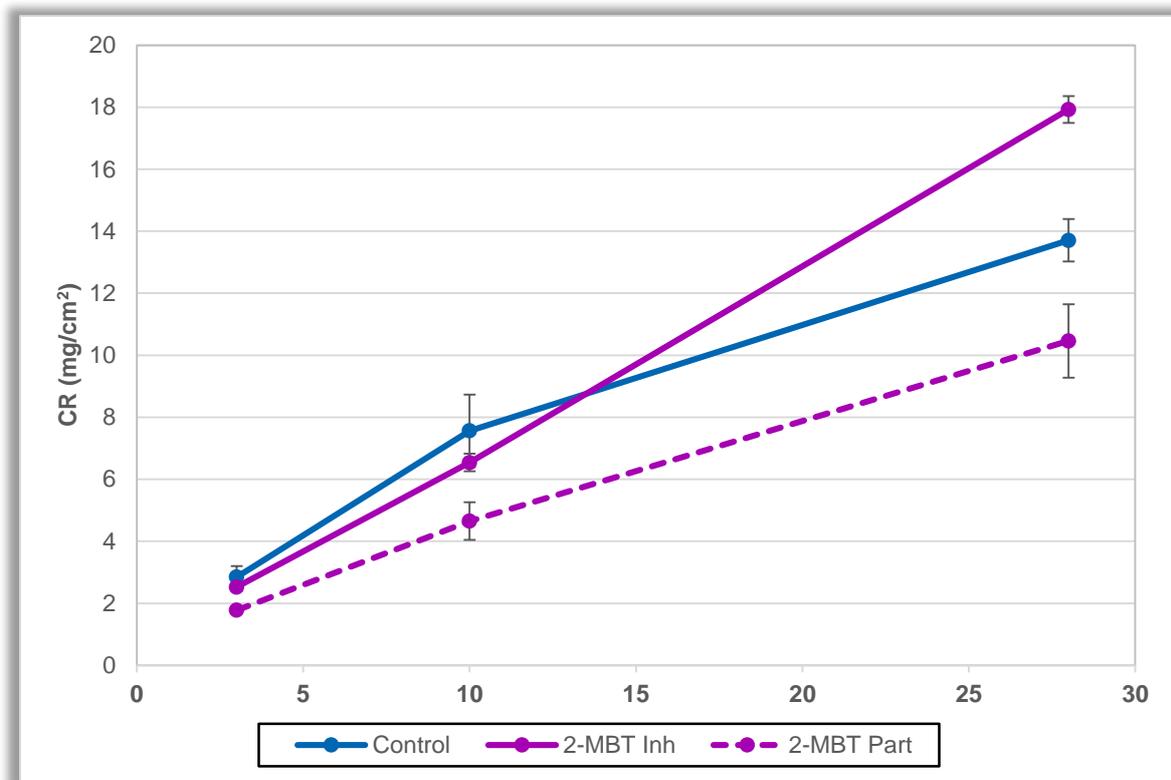


Figure 9: Corrosion rate of carbon steel in the presence of 2-MBT Inh, 2-MBT Part and Control as a function of immersion time

4. Conclusion

Three inhibitors were encapsulated into corrosion sensing microparticles. The total inhibitor content of 2-MBT in organic microparticles, could be modified over a wide range of concentrations whereby a formula with a reproducible loading of $55\% \pm 2\%$ was consistently achieved. The release of 2-MBT from organic microparticles in 0.01 M KOH solution was studied. 2-MBT was found to have a low 1 hour release which was followed by a continued release. Modification of the formula, not only the yielded particles with inhibitor payloads greater than 50% but also significantly increased the total inhibitor released as well as the time period of release up to 18 weeks.

Accelerated electrochemical and mass loss testing of all three inhibitors, both in their pure and encapsulated forms, was performed on carbon steel. Though it provided the steel with a homogeneous gray film, PPA was not able to reduce the corrosion rate in the mass loss testing and showed no significant inhibitive effects in polarization curves. 8-HQ Inh showed significant corrosion inhibition in the electrochemical testing but, in longer-term mass loss experiments, it proved to be ineffective. 8-HQ particles showed no differences to the Control samples in either tests. Similarly, 2-MBT inhibitor performed well during electrochemical testing, however, over the four weeks of immersion to measure mass loss, it was not able to provide significant corrosion protection. On the other hand, particles containing 2-MBT performed on par with 2-MBT in electrochemical testing but

also provided significant corrosion protection to carbon steel over the whole 28 days of salt solution immersion.

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