Self-Protecting Epoxy Coatings with Anticorrosion Microcapsules

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S.1 Carrier Solvent

The carrier solvent hexyl acetate was chosen among many solvents. Figure S1 shows the solubility of lawsone at room temperature. Lawsone is most soluble in DMF and DMSO. Both of which are highly polar solvents and are extremely difficult to encapsulate in a polymer microcapsule. The solubility of lawsone is less than 5 wt % in the rest of the solvents tested. Hexyl acetate was chosen because it has been previously encapsulated in literature and it is environmentally friendly. Hexyl acetate is used as a food additive because of its sweet smell.

![Figure S1: Solubility of lawsone in different solvents shown as a weight percentage.](image)

S.2 UV-vis Analysis

UV-vis spectroscopy was completed on various amounts of lawsone dissolved in methanol to determine the amount of lawsone contained within the microcapsules. A representative absorbance spectra is shown in Figure S2a. The peak has a wavelength of 333 nm. The calibration curve (Figure S2b) was made by mixing known concentrations of lawsone in methanol and measuring the corresponding absorbance peak. Microcapsule core extraction samples were made by submerging 50 mg of microcapsules in 18 mL of methanol for five days. This ratio of capsules to methanol was used to give an absorbance peak within the measurable range of the instrument. Five days was chosen as a sufficient extraction time based on initial experiments with type 5 capsules, in which no significant increase in the lawsone content was detected after three days (Figure S3). The dashed line is a line of best
fit and the error bar on the fifth day is one standard deviation. During this time, the lawsone was extracted from the microcapsule by swelling of the shell wall and then diffusion of the lawson through the shell wall. After the 5 days, the methanol solution was passed through a 0.4 µm syringe filter to remove all debris. UV-vis was then completed on the extracted core, and the lawsone concentration was calculated based on the calibration curve. With the known concentration, the lawsone weight percent was calculated and shown in Figure 4 and Table S1.

Figure S2: Microcapsule UV-vis analysis. (a) Lawsone absorbance spectra by UV-vis. (b) UV-vis calibration curve of peak amplitude at 333 nm vs. the known lawsone concentration.

Figure S3: Time dependent absorbance measurement of type 5 microcapsules. No significant increase was seen after the third day of submersion in methanol.
Table S1: UV-vis measured absorbance peak values

| Capsule Type | Absorbance Peak | Lawsone wt % |
|--------------|-----------------|--------------|
| Type 0       | 0.00 ± 0.015    | 0.01 ± 0.07  |
| Type 2       | 0.37 ± 0.027    | 1.68 ± 0.12  |
| Type 5       | 1.14 ± 0.044    | 5.23 ± 0.19  |
| Type 10      | 1.65 ± 0.049    | 7.56 ± 0.22  |
| Type 20      | 1.54 ± 0.025    | 7.06 ± 0.11  |

S.3 Speed of Sound Measurement

A free standing sample of the water-based epoxy coating material with arbitrary thickness was fabricated by spraying a glass substrate with a PTFE release spray prior to the coating application. The epoxy coating mixture was applied to the glass substrate and fully cured. After the curing procedure, the coating material was easily separated from the glass substrate.

A pulse-echo analysis was completed on the free standing samples. Figure S4 shows representative A-scans of the ultrasonic signal through the free standing sample (a) and of the reflected signal from the bottom of the water tank for a signal that does not pass through the sample (b). \( T_1 \) and \( T_2 \) are the times associated with the reflections from the top and bottom surface of the epoxy sample. \( T_3 \) is the time associated with the tank bottom reflection after it has passed through the sample. \( T_4 \) is the time associated with the tank bottom reflection of the ultrasonic signal that has not passed through the sample. Using the speed of sound in water \( (c) \), the thickness of the sample \( (d) \) is calculated by \( d = (cT_4 - cT_1 - c(T_3 - T_2))/2 \). The speed of sound \( (v) \) of the epoxy was then calculated by \( v = 2*d/(T_2 - T_1) \) and used for thickness measurements.

This point-wise analysis was completed over a large area of the sample and the velocity values were averaged. The average speed of sound for the epoxy was 2800 \( m/s \) with out capsules and was 2600 \( m/s \) for the epoxy sample with 20 wt % type 0 microcapsules.
Figure S4: A-scans used to measure the speed of sound of the epoxy coating material. (a) The ultrasonic signal through the free standing epoxy sample. (b) The ultrasonic signal of the tank bottom to be used as reference.

S.4 Thickness Analysis by Ultrasound and Scanning Electron Microscopy

The water-based coating material as applied is 47% water. As such, the fully cured coating thickness is much different from the applied thickness. Figure S5 shows that the difference between cured and applied thickness is quite significant. In some cases the cured thickness is less than 30% of the applied thickness due largely to the evaporation of water.

A sample SEM comparison image is seen in Figure S7. Figures S6 and S7 are images of epoxy coatings with 20 wt % type 0 capsules. Both coatings were applied at 355 µm and were allowed to fully cure. Figure S6 is a full field thickness plot of the coating. This specific coating has an average thickness of 118 ±8.5µm. Figure S7 shows a cross section of the coating after it has been polished. This specific coating has a thickness of 110 µm.

S.5 False Coloring of Optical Corrosion Images

False coloring of the visual corrosion images was completed because the color of the lawsone filled water-based epoxy coating is similar to the corrosion product. The area of the corrosion product was determined by subtracting out the background colors from the original images.
Figure S5: Cured thickness as a function of applied thickness for various samples. All samples were fabricated with a stoichiometric mixture of Epirez resin 6520-WH-53 and Epikure curing agent 6870-W-53 containing 53% solids and 47% water. An additional 20 wt% DI water was added for viscosity modification. Thickness measurements were made by ultrasonic testing (UT) or by SEM imaging of coating cross-sections. (Figure S8a-b). After subtraction, the resulting image represents the change in color due to the corrosion product (Figure S8c-d). Adding a red color to the corrosion product and showing it atop the original image results in the false colored image (Figure S8e-f).

S.6 Analysis of Undamaged Coatings

Undamaged water-based epoxy coatings with and without microcapsules were imaged with an optical microscope to observe the capsule distribution and to determine the presence any defects on the microscale. Microcapsules were shown to be uniformly disperse throughout the plane of the coating (Figure S9) and throughout the thickness (Figure S10). Optical cross-sectional images are difficult to acquire because the water-based epoxy coating material and capsule shell wall are transparent. Coatings with microcapsules were also observed to have a rougher surface then the coatings without microcapsules. It is obvious that the addition of the lawsone microcapsules give the coating its orange color. The coating material also looks orange because of the light diffracting as it passes through the coating. Small
Figure S6: Full field thickness plot of an epoxy coating with 20 wt% type 0 microcapsules measured by ultrasound. The average thickness of this coating is 118 ± 8.5 µm.

deformities were observed in coatings containing microcapsules that are likely due to air bubbles entrapped in the epoxy resin while incorporating the microcapsules. Coatings at low and high magnification are shown in Figure S11. Figure S11a-c show that there are no macroscopic defects in coatings with and without capsules. The water-based epoxy coating without capsules is optically clear so a high magnification image of the coating only shows the steel substrate with no defects in the coating. High magnification images of the coatings with type 0 (Figure S11d) and type 10 (Figure S11e) microcapsules show microscopic defects in the coatings. These defects are only slightly larger then the microcapsules.

Imaged water-based epoxy coatings were submerged in a 5 wt % NaCl solution for five days and optically imaged (Figure S12). Corrosion of the substrate did occur within the observed microscopic defects discussed previously. Coatings with capsules both had a similar amount of defects however the coating with type 0 capsules showed more corrosion product deposited on the surface of the coating near the defects after the corrosion analysis then the coating with type 10 capsules. High magnification images in both corroded samples showed corrosion near the previously observed defects.

The electrochemical analysis that was used on the damaged samples was also completed.
on the undamaged samples to determine the change in barrier properties of the water-based epoxy coating with microcapsules. Electrochemical results are shown in Figure S13. No potential or current was measurable for the coating without capsules. The area of the exposed steel for these samples is unknown because there was no inflicted damage to the coatings and only small defects from the manufacturing process. Therefore corrosion current densities could not be measured. The open circuit potential for the control and self-protecting coating were not statistically different and were around -300 mV which is different than the coatings with inflicted scribe damage, -550 mV. Similarly, the corrosion current was not statistically different for the two samples, indicating that their initial state before scribe damage is the same regardless of their type of capsule. The magnitude of the corrosion current is also much smaller than samples with inflicted scribe damage. The inflicted scribe damage had corrosion currents on the order of micro Amps, but the undamaged coating has corrosion currents on the order of nano Amps.

The observed deformities in the coatings with microcapsules did change the native barrier properties of the coating material, but they were determined to not have an effect on the self-protecting results. Both the control (type 0 capsules) and the self-protecting (type 2, 5, 10 and 20 capsules) coatings started at the same initial state with a similar amount of defects. Using a coating without capsules would not be an appropriate control because its
initial state is different from a coating with microcapsules.
Figure S8: Original and false colored images of the optical corrosion results. (a-b) Original corrosion images. (c-d) Regions of corrosion that were false colored. (e-f) Final corrosion images with false coloring. (a,c,e) Coatings with type 0 capsules, and (b,d,f) are coatings with type 10 capsules.
Figure S9: Optical microscope image of water-based epoxy coatings containing type 0 (a) and type 10 (b) capsules showing a uniform capsule distribution.

Figure S10: Optical microscope images of freeze fractured water-based epoxy coatings applied to a glass substrate. (a) Coating without microcapsules. (b) Coating containing 20 wt % type 0 capsules. (c) Coating containing 20 wt % type 10 capsules.
Figure S11: Optical images of water-based epoxy coatings before the visual corrosion assessment. (a) Coating without microcapsules. (b) Coating containing 20 wt % type 0 capsules. (c) Coating containing 20 wt % type 10 capsules. (d) Micron-scale defects in a coating with 20 wt % type 0 capsules. (e) Micron-scale defects in a coating with 20 wt % type 10 capsules.
Figure S12: Optical images of water-based epoxy coatings after the visual corrosion assessment. (a) Coating without microcapsules. (b) Coating containing 20 wt % type 0 capsules. (c) Coating containing 20 wt % type 10 capsules. (d) Corrosion product on the surface of the coating near the micron-scale defects in a coating with 20 wt % type 0 capsules. (e) Corrosion product on the surface of the coating near the micron-scale defects in a coating with 20 wt % type 10 capsules.
Figure S13: Electrochemical corrosion potential (a) and corrosion current (b) of water-based epoxy coatings without any inflicted scribe damage. The control coatings contained 20 wt % type 0 capsules and the self-protecting coatings contained 20 wt % type 10 capsules.