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# Self-Healing Epoxy Coating with Microencapsulation of Linseed Oil for the Corrosion Protection of Magnesium (Mg)

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**Abstract.** The ability to self-heal is an important feature for the long-term durability of protective coatings on metal alloys. Microcapsules in the self-healing coating allowed for automatic recovery of any damages or cracks, extending the life of the coating. In this study, self-healing microcapsules containing linseed oil as the core material and polyurea-formaldehyde (PUF) as the shell material were manufactured to epoxy resin matrix. Coatings were applied to a bare magnesium (Mg) substrate and scratched to test the self-healing ability. Optical and scanning electron microscopy (SEM) were used to characterize the microcapsules formed by varied stirring rates of 300 and 800 rpm. By using potentiodynamic polarization in a 3.5 wt.% NaCl solution, the corrosion rate of embedded microcapsules and coatings on Mg was evaluated, and the corrosion rate was studied using the Tafel plot. As a consequence, the epoxy coating containing linseed oil and urea formaldehyde, stirred at 800 rpm, significantly resists corrosion attack on the magnesium sheet, with decreased corrosion current density,  $i_{corr}$  ( $1.552 \mu\text{A}/\text{cm}^2$ ) as compared to the bare magnesium sheet ( $109.8 \mu\text{A}/\text{cm}^2$ ). During the microcapsule preparation, increasing the stirring rate from 300 to 800 rpm reduces the  $i_{corr}$  value by roughly half. As a result, the self-healing coatings demonstrated adequate self-healing and corrosion resistance recovery on magnesium alloys.

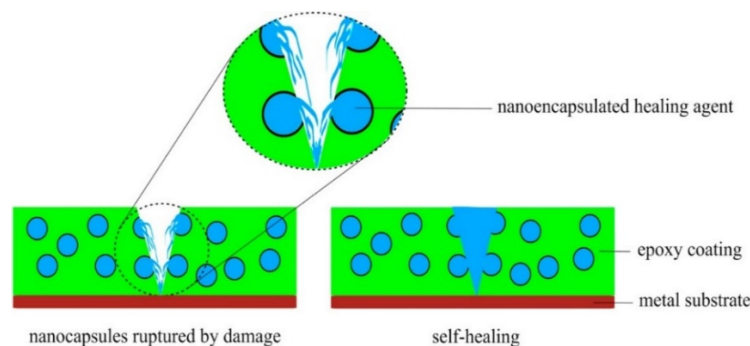
## 1. Introduction

Coatings are the most common method to control metal substrate's degradation from the corrosive environment. The application of coating is useful when other ways, such as selection of materials, design and control of the environment are minimal. Coatings can be applied to any material (inorganic, metallic or organic) and are effective for prevention of corrosion in a wide range of industries, including the automobile, marine, infrastructure, aerospace, telecommunications, food and drink [1–5]. One of the most common and effective methods of protecting bare metal from oxidation has been the application of organic coatings [2,6,7]. Nevertheless, organic coatings are subjected to mechanical damage which can cause coating failure and then water will penetrate through the coating and cause corrosion of the metal [8,9]. As a result, the self-healing coating concept was proposed as a rapid solution for mechanical damage [10,11].



Self-healing coating ability is needed to enhance their long-term durability and reliability, in particular for protective coatings. Self-healing coating capacity is necessary, especially for protective coatings, to improve long-standing durability and reliability. Different forms of problems in protective coatings could be created by age, unavoidable collisions, cracks, and ruptures produced by external forces, which might then spread, lead to faster coating degradation, severely reduce service life, and possibly have disastrous consequences [12,13]. Self-healing research with the use of microcapsules as a corrosion inhibitor has received significant stimulation as self-healing developments are being developed by in situ polymerisation [10,14–18]. Figure 1 depicts the schematic illustration of self-healing repairability by adding oil-based corrosion inhibition agent in the polyurea formaldehyde (PUF) [18]. The healing agent is typically encapsulated by urea and formaldehyde by in situ polymerization. This solvent-free technology features a simple approach, cheap cost, and is straightforward to industrialise when compared to other encapsulation approaches. Another advantage of this technology is that the microcapsule size and shell thickness may be controlled [19,20]. In a nutshell, the process involves creating a stable oil-in-water emulsion with the help of emulsifiers, followed by the formation of a polymer shell or wall surrounding the dispersed oil drops by polymerizing the oligomers interfacial [16,21].

An autonomous healing mechanism or extrinsic healing system is created by including polymerizable healing agents or corrosion inhibitors into the coating matrix. In many cases, microcapsules store these healing agents. When the coating is damaged, the capsule ruptures and releases the healing agents, which polymerize to create a protective layer, restoring the coating's barrier property [22]. Traditional polymers, such as epoxy, polyester, vinyl ester, and others, which are employed in lightweight engineering structures such as aircraft, do not have form memory capabilities. Although they can be turned into memory polymers (SMPs) by reducing cross-link density, they lose structural abilities such as strength and stiffness and have limited memory capacity [4,23–25].



**Figure 1.** Self-healing repairability by added oil-based corrosion inhibition agent in the polyurea formaldehyde (PUF) [18].

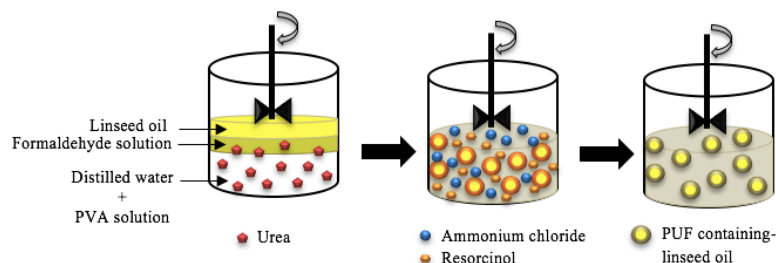
## 2. Materials and Methods

The microcapsules were synthesized by mixing a corrosion inhibitor agent consisting of linseed oil, urea-formaldehyde, resorcinol, ammonium chloride, polyvinyl alcohol (PVA). An in-situ polymerization method is applied for the preparation of microcapsules. Initially, 200 ml of distilled water (DI) and 7.5 ml of 5 wt.% aqueous solution of polyvinyl (PVA) were mixed in a 500 ml beaker. Under an agitation rate of 300 rpm, 50 ml of linseed oil is added dropwise into the aqueous solution to form a stable oil-in-water emulsion. Urea-formaldehyde is applied as shell material by mixing 7.5 g of urea and 19.02 g of 37 wt.% formaldehyde aqueous solution. Then, 0.75 g ammonium chloride and 0.75g resorcinol were added to the mixture and stirred for 1 hour till it dissolved in the mixture. Then, the pH of the emulsion was adjusted to approximately 3 by a few drops (2-3 drops) of 1 wt.% hydrochloric acid aqueous solution. The pH was confirmed by using a pH meter.

The mixture solution was mechanically stirred by using a hot plate and magnetic stirrer, and the stirring rate was performed at 300 rpm for 1-hour duration. The next mixture solution was prepared following the same method, but by using an 800-rpm stirring rate. All the chemicals were purchased from Sigma-Aldrich as AR grade chemicals. The ingredients were weighted by using an analytical balance to get a precise measurement of each ingredient. The microcapsules were then vacuum filtrated and placed on the filter paper before rinsed with distilled water to remove any suspended oil, and further dried at ambient temperature for overnight. The schematic illustration of microcapsules preparation by in-situ polymerization is shown in Figure 2. Characterization of the microcapsules including the size, and shell thickness was performed by optical microscopy and measured by ImageJ software.

Epoxy resin, E101 and hardener were prepared for self-healing coating with a ratio of 3:1. The microcapsules were carefully added to the epoxy by 10% weight. AZ31 magnesium substrates with a dimension of 30 mm x 40 mm and a thickness of 2 mm were rinsed and pre-cleaned with acetone. The Mg substrate was prepared by mechanical ground to 1200 grit before application of coating on the surface. The coating was applied on the Mg substrate by using a small scraper to make sure a thin coating layer is produced. The coating was then allowed to cure for 7 days in ambient air.

The scratch test was carried out by manually cutting the coating surface with a thin blade. The scratched sample was then observed by Olympus optical microscopy and Hitachi TM3030 Plus scanning electron microscope (SEM). The sample before and after exposure to 120 hr was observed to determine the self-healing performance. The corrosion resistance of bare AZ31 Mg substrate, epoxy with embedded microcapsules coatings were evaluated by potentiodynamic polarization tests at 3.5 wt.% NaCl (aq) at room temperature using a Gamry FAS2 Fentostat equipment. A typical three-electrode cell was used; an Ag/AgCl electrode as reference electrode, and graphite as counter electrode and the tested samples as working electrode. Before each measurement, the samples were immersed in the electrolyte for 10 min to test the open circuit potential ( $E_{oc}$ ). A potentiodynamic polarization test was conducted on the sample by applying a potential range of -2 to -1.1 V versus Ag/AgCl at a scan rate of 1 mV/s. The corrosion potential ( $E_{corr}$ ) and corrosion current density ( $i_{corr}$ ) were determined using the Gamry software.



**Figure 2.** Schematic illustration of preparation of microcapsules by in-situ polymerization.

### 3. Results and Discussions

#### 3.1 Microcapsule Formulation

The effect of stirring rate on the size distribution of microcapsules was investigated by measuring the diameter of a microcapsule in the ImageJ software, and a lower stirring rate induces large microcapsule size and unstable shell formation. Thus, it is possible to control the size of the microcapsule by controlling the stir rate and reaction time. Less reaction time may influence shell formation as it may leads to incomplete shell formation and surface rupture. Hence, formation and stabilization of emulsion are very crucial to developing self-healing microcapsules for corrosion inhibitors. It is greatly affected by the stir rate and concentration of emulsifier [26–28]. The incomplete formation of shell microcapsule could not store self-healing agent and release the agent when conducting a scratch test. However, the incomplete shell formation also releases the agent but the percentage of self-healing is not completely optimum [29].

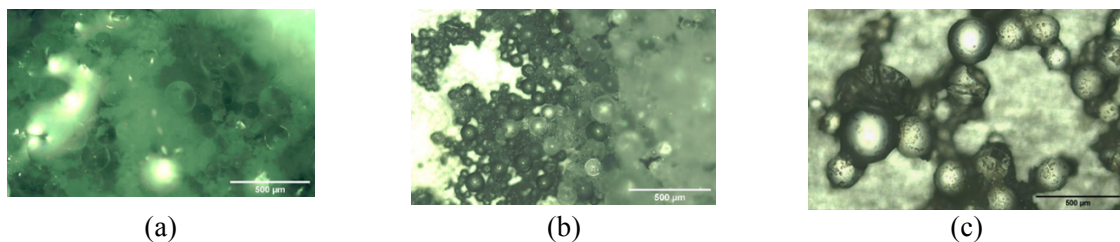
A microcapsule with a stirring rate of 300 rpm has no suspended solution but the longer the mixture is held before filtration, the mixture is not fully emulsified and unstable. The texture of the mixture was a milky white/beige solution and after washing and drying, the microcapsule was in white free-flowing powder. The formation of microcapsule stirred at a stir rate of 300 rpm is shown in Figure 3. The microcapsules are in spherical form as characterized under optical microscopy. Stirring is intended to form a stable emulsion by splitting large droplets of oil into smaller droplets of oil. At low stirring speed, oil droplets agglomerated and formed an unstable emulsion [30].

### 3.2 Microcapsule Characterization

In-situ polymerization was used to create microcapsules containing linseed oil and a corrosion inhibitor ingredient. The optical micrographs in Figures 4(a) and (b) depict the distribution of spherical microcapsules stirred at 300 and 800 rpm, respectively, and seen in the bright field mode of the optical microscope. Figure 4(c) shows a considerably clearer micrograph of microcapsules, allowing us to view the surface morphology of the microcapsule. The dark circle surrounding the microcapsules with a clear dot indicates the microcapsules' core/shell structure with compact encapsulation.

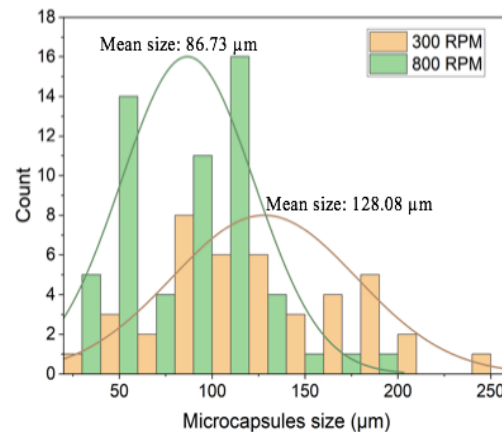


**Figure 3.** Microcapsules of polyurea-formaldehyde (PUF) with linseed oil as a corrosion inhibitor agent, stirred at a stirring rate of 300 rpm.



**Figure 4.** Optical micrograph of the distribution of the spherical microcapsules (a) stirred at 300 rpm, (b) 800 rpm and (c) magnified microcapsules

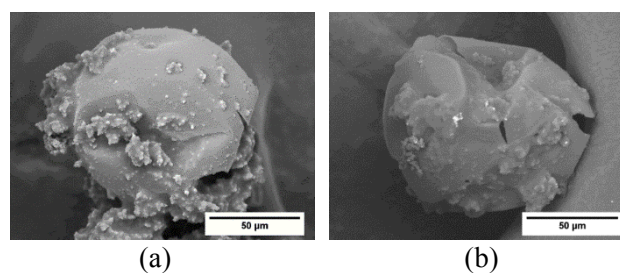




**Figure 5.** Histogram chart with mean size of microcapsules stirred at 300 and 800 rpm.

Microcapsules stirred at 300 rpm ranged in size from 26.43 to 253.30  $\mu\text{m}$ . While microcapsules stirred at 800 rpm range in size from 30.83 to 187.23  $\mu\text{m}$ . The mean size of microcapsules stirred at 300 rpm is 128.08  $\mu\text{m}$ , while the diameter of microcapsules swirled at 800 revolutions per minute is 86.73  $\mu\text{m}$ . The histogram chart in Figure 5 illustrates the distribution of microcapsule sizes. [31] observed that increasing the stirring rate reduces the size of the microcapsules and also the optimal core: shell ratio. [30] confirmed this conclusion, showing that stirring at a speed of 500–1500 rpm is the optimal speed for obtaining microcapsules with a size smaller than 100  $\mu\text{m}$ .

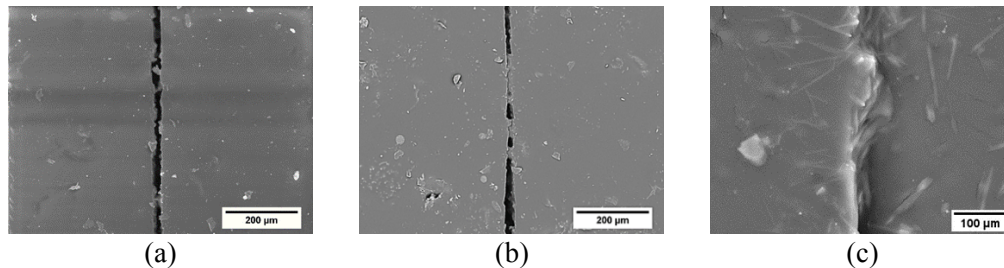
Figures 6(a) and 6(b) show SEM images of microcapsules in spherical form. A rough surface can be observed from the images. The dried microcapsules were observed to be ruptured during SEM observation. The microcapsules can also crack/rupture during filtration and stirring if the interface between the inorganic components and the shell is not compact, allowing the microcapsules' core substance to easily leak out [16]. The surface of the microcapsule is relatively rough and porous, which may allow for substantial interface interactions between the microcapsules and the coating matrix [32,33]. The nonporous structure could minimise the diffusion and permeability of the encapsulated liquid healing agent to keep it in microcapsules till it breaks up [34].



**Figure 6.** SEM images of microcapsules with rough surfaces that ruptured during observation.

All samples were exposed to the ambient environment for 120 hrs (5 days). While the sample containing microcapsules and epoxy demonstrates homogenous microcapsule diffusion throughout the coating as observed from the fine coating after 120 hours of exposure. Because the ambient environment is not corrosive, the corrosion reaction of the scratched coating with the environment may not be as visible, and the scratches were clean and free of corrosion products. It is evident that coating does self-healed and provides better resistance even after scratching. The SEM images of a scratched coating, and self-healing coating after 120 hrs are shown in Figures 7(a) and (b). The magnified image in Figure 7(c) confirms the self-healing region of coating with most of the scratch is recovered and healed. This demonstrates that the linseed oil was cross-linked to form a solid film and was released to automatically

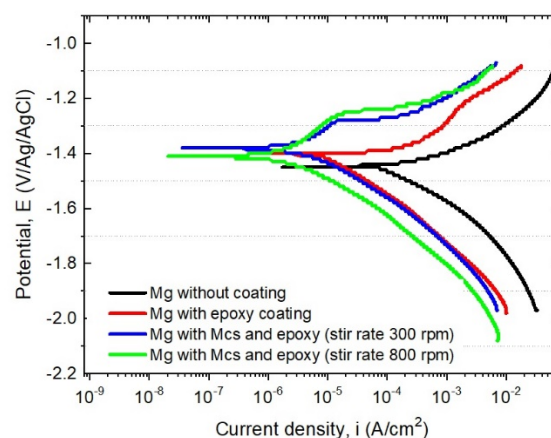
cover the scratch on the coating surface. This is because linseed oil contains a significant amount of unsaturated fatty acids, made up of double bonds of carbon-carbon [10,16]. It is expected that the released linseed oil will dry via auto-oxidation processes in contact with the environment and partially fill the scratched area [30].



**Figure 7.** SEM images of (a) fully scratched sample of Mg, (b) partial self-healed coating and (c) magnified self-healed coating.

### 3.3 Corrosion Evaluation by Electrochemical Measurement

The electrochemical kinetics of the coating was analysed by Tafel plot. The corrosion resistance of the sample can be estimated using the corrosion current density,  $i_{corr}$  values from the Tafel plot, which represents the flow of electrons from the magnesium to the surrounding solution [35,36]. Figure 8 represents the Tafel plot for magnesium substrate, epoxy coated Mg, sample of self-healing coated with microcapsules stirred at 300 rpm and self-healing coated with microcapsules stirred at 800 rpm immersed in 3.5 wt.% NaCl solution. During the in-situ polymerization of microcapsules preparation, the corrosion current density,  $i_{corr}$ , decreases as the stirring rate increases. The  $i_{corr}$  value for magnesium substrate is  $109.8 \times 10^{-6} \text{ A/cm}^2$ , while the value for epoxy coated sample is  $25.53 \times 10^{-6} \text{ A/cm}^2$ . The coated magnesium with microcapsules and the magnesium substrate both had much lower  $i_{corr}$  values. The  $i_{corr}$  value of a coating stirred at 300 rpm is  $3.059 \times 10^{-6} \text{ A/cm}^2$ , and the  $i_{corr}$  value of a coating stirred at 800 rpm is  $1.552 \times 10^{-6} \text{ A/cm}^2$ , representing a nearly 99% reduction in  $i_{corr}$  over bare magnesium. Table 1 displays the Tafel plot data for all of the samples. The potential value is shifted towards a positive value by applying a coating to the magnesium sample. All coatings, including epoxy coatings without microcapsules, exhibit passivity. Both the coated magnesium with microcapsules (self-healing coating) exhibit lower passivity current density than that of epoxy coating, indicating that the passive film formed on self-healing coating has higher corrosion resistance than the single epoxy coating, which is consistent with the result of  $i_{corr}$  [17].



**Figure 8.** Tafel plot of magnesium samples in different coatings conditions immersed in 3.5 wt.% NaCl solution.

**Table 1.** Data of corrosion current density and potential of magnesium sample based on Tafel plot.

Sample	E <sub>corr</sub> (V)	i <sub>corr</sub> (A/cm <sup>2</sup> )
Bare Mg substrate	-1.48	109.8 x 10 <sup>-6</sup>
Epoxy coated Mg	-1.492	25.53 x 10 <sup>-6</sup>
Self-healed coated Mg with microcapsules (300 rpm)	-1.398	3.059 x 10 <sup>-6</sup>
Self-healed coated Mg with microcapsules (800 rpm)	-1.428	1.552 x 10 <sup>-6</sup>

#### 4. Conclusions

This study generally presented the formulation method to produce smart coating against corrosion of magnesium and its alloys, specifically by self-healing epoxy coating and encapsulated linseed oil as the corrosion inhibitors. We explored the formulation to produce self-healing coating by varying the stirring rate, and evaluated the corrosion resistance of magnesium by the self-healing coatings. The results indicated that:

- 1) Microcapsules mean size is reduced from 128.08 to 86.73  $\mu\text{m}$  with the increase in stirring rate during in-situ polymerization from 300 to 800 rpm.
- 2) The corrosion resistance of self-healing coating increases, by increasing the stirring rate to 800 rpm. The corrosion current density value, i<sub>corr</sub> of coated sample with microcapsules (stirred at 800 rpm) reduces to more than 99%, with i<sub>corr</sub> of 1.552  $\mu\text{A}/\text{cm}^2$ , as compared to bare magnesium substrate with i<sub>corr</sub> of 109.8  $\mu\text{A}/\text{cm}^2$ . Thus, the self-heal coating sample excellently protects the corrosion of magnesium.

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