Self-Healing Abilities of Shape-Memory Epoxy-Contained Polycaprolactone Microspheres Filled with Cerium(III) Nitrate Coated on Aluminum 2024-T3

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ABSTRACT: The shape-memory epoxy (SME) mixed with 10 wt % polycaprolactone (PCL) microspheres containing 5% cerium(III) nitrate (Ce(NO₃)₃) (PCL5Ce) was coated on an aluminum plate 2024-T3 to investigate the self-healing property. The coating was scratched and heated at 80 °C for 30 min to activate the self-healing mechanism and compare with a nonscratched coating. Surface morphology was investigated by scanning electron microscopy. The scratch was completely healed by the PCL5Ce via a thermally assisted self-healing process. Based on electrochemical impedance spectroscopy, the postheated scratched coating had shown impedance values close to the nonscratched coating, which indicated that corrosion resistivity was restored. Ce(NO₃)₃ content at the scratched area was analyzed by focused ion beam–scanning electron microscopy. The scratch width was healed and filled with Ce(NO₃)₃. Therefore, PCL5Ce is capable of being used as an enhancing additive for the self-healing performance in SME coating.

1. INTRODUCTION

Corrosion is a major problem for various industries and causes damage to structures and facilities made of metal. Generally, damage starts on the surface and propagates deeper into the substrate and/or spreads wider. Metal surfaces have to be protected and the most common measure against corrosion is to apply protective coatings. Advancements in anticorrosion coating technologies are currently focusing on smart coatings (self-repairing/healing, self-cleaning, self-stratifying/assembly, self-lubricating, and self-dimming coatings) to control the reaction rate by inhibiting or stopping the corrosion initiation process.1−4

Recently, self-healing coatings which consist of a shape-memory epoxy (SME) and microspheres containing self-healing agents are intensively researched in corrosion prevention.1−9 The SME is a smart material that has the ability to recover from a temporary deformation to its original permanent shape because of entropically driven processes assisted by an external thermal stimulus.10,11 Microspheres are purposely used as a carrier to control the release of self-healing agents contained inside.5−9 Several reports demonstrated that microsphere carriers made from polycaprolactone (PCL) have dominant advantages such as high strength, slow degradation, high compatibility, high elasticity, and inexpensiveness.12−16 In addition, cerium(III) nitrate (Ce(NO₃)₃) is a well-known corrosion inhibitor, especially for aluminum alloys.17 This is due to the fact that cerium(III) cations (Ce³⁺) are capable of passivating any scratches or marks on the substrate by the formation of cerium hydroxide.17−21

The self-healing coating has an ability to recover from any light superficial damage or suppress any corrosion initiations of metal substrates. In turn, self-healing coatings reduce the degradation of coating materials, prolong service life of coating materials, and reduce the repair cost of coating materials in industries that encounter corrosion.18,22−26 Even if this concept seems to be promising, the key achievement in smart coatings is the stability of carriers that contain self-healing agents, which depends on the preparation techniques.12−18 Among those techniques, a double emulsion evaporation (DEE) technique is of interest because it can be used to encapsulate the corrosion inhibitors with high efficiency.27−29

Hence, this research focuses on the investigation of the self-healing ability of an SME mixed with PCL microspheres containing Ce(NO₃)₃ as a self-healing agent coated on aluminum 2024-T3 plates. The DEE technique was used to produce the self-healing microspheres and later mixed with SME. The self-healing properties including thermal healing
temperature, shape-memory effect, and surface morphologies were investigated in this study. Furthermore, the corrosion resistance was also discussed using electrochemical impedance spectroscopy (EIS).

2. EXPERIMENTAL PROCEDURE

2.1. Materials. The metal substrates used in this study were aluminum alloy 2024-T3 plates with dimensions of 60 mm × 80 mm × 0.5 mm. For microsphere preparation, a carrier (PCL) and a self-healing agent (Ce(NO3)3) were from Sigma-Aldrich and Sinopharm Chemical Reagent, respectively. In addition, the organic solvent [dichloromethane (DCM)] was from Beijing Shiji. Also, polyvinyl alcohol (PVA) used as an emulsifier was from Xiya Reagent. For the SME preparation, an epoxy monomer (bisphenol A diglycidyl ether), a curing agent [poly(propylene glycol) bis (2-aminopropyl ether) (Jeffamine D230)], and a hardener (decylamine) were from Sigma-Aldrich, Shanghai Aladdin Bio-Chem Technology, and Xiya Reagent, respectively. All chemicals were used as received and without further purification. The chemical structures for each reagent to make SME are shown in Figure 1.

![Figure 1. Chemical structures of the SME.](https://example.com/figure1)

2.2. Microsphere Preparation. PCL microspheres were synthesized with two different percentages of Ce(NO3)3, 5% and 10% (PCL5Ce and PCL10Ce), using the DEE technique. To create a single emulsion (w1/o) of PCL5Ce, the water phase (w1) was prepared by dissolving 0.025 g of Ce(NO3)3 in 5 mL of 0.15% w/v PVA. The oil phase (o) was prepared by dissolving 0.475 g of PCL in 15 mL of DCM. For PCL10Ce, 0.05 g of Ce(NO3)3 was dissolved in 0.15% w/v PVA and 0.5 g of PCL in 15 mL of DCM for the water phase and oil phase, respectively. All solutions were left for 30 min until fully dissolved. The o phase was added to the w1 phase and then homogenized for 5 min at 25,000 rpm. Then, the homogenized solution was combined with 95 mL of 0.15% w/v PVA solution (w2) and stirred using a magnetic stirrer at 50 °C for 10 h. This created the double emulsion (w1/o/w2). Microsphere particles were dispersed in PVA solution after stirring. Afterward, the stirred mixture was centrifuged at a speed of 3000 rpm for 5 min to evaporate the PVA solvent. Then, the precipitated microspheres were combined with deionized water and centrifuged at 5000 rpm for 5 min. This removed the remaining PVA solvent. Precipitated microsphere particles were then separated after being centrifuged. Thereafter, they were frozen in a freezer for 2 h and then freeze-dried using a vacuum dryer for 24 h. Finally, the self-healing microspheres were completely synthesized.

![Figure 2. SEM images of (a) PCL0Ce, (b) PCL5Ce, and (c) PCL10Ce synthesized using the DEE technique.](https://example.com/figure2)

Figure 2 shows the particle size of PCL microspheres. The average particle sizes were 3.81 μm (Figure 2a), 6.08 μm (Figure 2b), and 24.75 μm (Figure 2c) obtained without Ce(NO3)3 (PCL0Ce), with 5% Ce(NO3)3, and with 10% Ce(NO3)3, respectively. Thus, the particle size of the PCL microspheres increased with the addition of Ce(NO3)3. PCL0Ce and PCL5Ce microspheres were smooth and spherical but PCL10Ce showed some particle disintegration. Energy-dispersive X-ray spectroscopy (EDX) was used to measure the distribution of cerium content in each microsphere. EDX results showed PCL5Ce being evenly diffused into all microspheres with a content distribution of 0.06–
0.07% on average. EDX results for PCL10Ce showed only partial diffusion. Various particle sizes contained equal amounts of Ce(NO$_3$)$_3$. Thus, smaller particles contained higher amounts of Ce(NO$_3$)$_3$ per specific volume as compared to the bigger particles. Therefore, the smaller particles were more effective in improving the self-healing property. PCL0Ce and PCL5Ce were chosen for coating preparation.

### 2.3. Coating Preparation and Application

In this research, three different coatings were applied on aluminum 2024-T3 plates: (i) pure SME, (ii) SME added by PCL0Ce (SME-PCL0Ce), and (iii) SME added by PCL5Ce (SME-PCL5Ce).

Aluminum 2024-T3 plates were polished by abrasive papers (150 and 240 grit) and later cleaned with ethanol in an ultrasonic bath.

The pure SME was prepared using a mixture of 2.27 g of bisphenol A diglycidyl ether, 0.192 g of poly (propylene glycol) bis (2-aminopropyl ether), and 0.787 g of decylamine. Then, it was mixed until it became homogeneous. Two types of SME coatings with microspheres were prepared by adding 0.361 g of PCL0Ce and PCL5Ce to the SME, respectively. Afterward, the coatings were immediately applied to the surface of aluminum 2024-T3 plates using a wire-wound rod with a thickness of 150 μm. The coated aluminum samples were placed in a vacuum oven at a curing temperature of 55 °C for 24 h.

#### 2.4. Characterizations

For determining the self-healing property, the surface of the coated specimens was scratched through the coating layer with an approximate length of 1 cm using a sharp blade. The average gap of the scratch was approximately 20–40 μm. Then, the scratched specimens were heated at 80 °C for 30 min in a vacuum oven. Surface morphologies before and after scratching were observed by scanning electron microscopy (SEM) (Quanta, FEI 250). The Ce(NO$_3$)$_3$ content at the scratched area was analyzed by focused ion beam (FIB)–SEM (Tescan, Lyra 3) and EDX (Quanta, FEI 250).

For determining the thermal property, the coated specimens were characterized by differential scanning calorimetry (DSC). The conditions for the thermal measurements were under nitrogen at a heating rate of 10 °C min$^{-1}$. The thermal instrument was made by TA Instruments (DSC Q2000).

For determining the corrosion resistance, a conventional three-electrode electrochemical cell in a Faraday cage was used to perform electrochemical measurement. The coated specimen, the platinum foil, and the saturated calomel electrode were used as the working electrode, the counter electrode, and the reference electrode, respectively. EIS measurements were performed in the 3.5 wt % NaCl electrolyte solution at room temperature using a potentiostat from Princeton Applied Research (PARSTAT 2273). The frequency range used for the EIS measurement was from 10$^5$ to 10$^{-2}$ Hz with a sinusoidal perturbation of 20 mV (DC Potential) and at open-circuit potential.

### 3. RESULTS AND DISCUSSION

#### 3.1. Thermal Property

The thermal property of the pure SME and SME-PCL5Ce was characterized by DSC. All the cross-linked epoxy polymers with glass transition temperatures ($T_g$) above room temperature were found to possess shape-memory properties. The $T_g$ of SME was determined to be the inflection temperature, and the melting temperature ($T_m$) value was obtained from the endothermic peak in the DSC curve. Figure 3 shows the DSC curves from which the appropriate heating temperatures can be determined based on the $T_g$ and $T_m$ values. The inflected regions near 35 °C and 40 °C reflect the glass transitions of the pure SME and SME-PCL5Ce, respectively. A sharp endothermic peak is observed at around 50 °C, which corresponds to the $T_m$ of the SME-PCL5Ce coating.

#### 3.2. Healing Temperature

After the aluminum 2024-T3 plates were coated by SME-PCL5Ce, they were scratched and heated at varied temperatures (60, 65, 70, 75, and 80 °C) to determine a suitable temperature that activates the self-healing mechanism.

A temperature of 80 °C was chosen as a healing temperature where microsphere particles melted and the scratch closure was at 100% healing (completely healed) as presented in Figure 4. Optical microscope (OM) images in Figure 4b show that the scratch width after heating at 80 °C for 30 min was completely closed compared with the original width shown in Figure 4a.

Figure 4. Optical microscope (OM) images of (a) before 80 °C for 30 min and (b) after 80 °C for 30 min.

#### 3.3. Shape-Memory Effect

The original shapes of pure SME samples are shown in Figure 5a1,b1 and their shapes after mechanical deformation are shown in Figure 5a2,b2. The
shape of the deformed samples after heating 55 °C for 30 min and 80 °C for 30 min are shown in Figure 5a3, b3, respectively. The samples at both temperatures were compared to their original shape. Therefore, the shape-memory effect can be activated at 55 °C and 80 °C.

3.4. Surface Morphologies. 3.4.1. Scratched Coating Surface. The original scratch width before heating was approximately 20–40 μm, as shown in Figure 6a1, b1, c1 for pure SME, SME-PCL0Ce, and SME-PCL5Ce, respectively. The samples were then heated and scratch widths were measured. The scratch width of the pure SME decreased because of the shape-memory effect but remained open, as shown in Figure 6a2. In Figure 6b2, the scratch width of SME-PCL0Ce was filled and overflowed with the melted PCL microspheres but was not completely healed. The scratch width of SME-PCL5Ce was closed and completely healed, as shown in Figure 6c2. It was successful in the close-then-heal process which consists of (i) the scratch closing by the shape-

Figure 5. Effect of heating temperatures on pure SME; (a) at 55 °C [(a1) original shape, (a2) after mechanical deformation, and (a3) after heating at 55 °C for 30 min] and (b) at 80 °C [(b1) original shape, (b2) after mechanical deformation, and (b3) after heating at 80 °C for 30 min].

Figure 6. SEM images of the self-healing mechanism before heating (BH) and after heating (AH) at 80 °C for 30 min: (a1) pure SME-BH, (a2) pure SME-AH, (b1) SME-PCL0Ce-BH, (b2) SME-PCL0Ce-AH, (c1) SME-PCL5Ce-BH, and (c2) SME-PCL5Ce-AH.
memory effect of the epoxy and (ii) release of Ce\(^{3+}\) to fill and heal the scratched surface\(^{30–32}\).

### 3.4.2. Coating Cross Section.

The SME-PCL5Ce coating after the self-healing process was evaluated for Ce(NO\(_3\))\(_3\) distribution by FIB–SEM analysis. It proved that the scratch width was completely healed and was filled by the Ce(NO\(_3\))\(_3\) self-healing agent, as shown in Figure 7a. In Figure 7b, EDX results show the percentage of cerium content after the crack was healed which confirmed the capability of Ce(NO\(_3\))\(_3\) as a self-healing agent.

### 3.5. Electrochemical Measurement.

Corrosion resistance of the coatings was characterized by EIS results. All coated aluminum 2024-T3 plates were scratched with a width of approximately 20–40 \(\mu\)m and immersed in a 3.5 wt % NaCl solution.
solution. The scratched aluminum 2024-T3 plates were tested after immersion times of 0 h, 1, 3, 5, and 7 days.

The Bode and Nyquist plots are shown in Figures 8 and 9, respectively. The Bode results of the scratched coating samples of pure SME, SME-PCL0Ce, and SME-PCL5Ce without heating are shown in Figure 8a1,b1,c1, respectively. In addition, the Bode results of the scratched coating samples of pure SME, SME-PCL0Ce, and SME-PCL5Ce after the self-healing process (with heating) are demonstrated in Figure 8a2,b2,c2, respectively. Furthermore, the Nyquist results of the scratched coating samples of pure SME, SME-PCL0Ce, and SME-PCL5Ce after the self-healing process (with heating) are depicted in Figure 9a,b,c, respectively. To determine the corrosion resistance of the coating, low-frequency impedance modulus \( |Z|_{0.01\text{Hz}} \) of the Bode plots was analyzed and investigated. The high \( |Z|_{0.01\text{Hz}} \) values of the nonscratched coating after the self-healing process were used as a good coating reference to compare with the scratched samples after heating, as shown in Figure 8a2,b2,c2.

After heating the SME-PCL0Ce and SME-PCL5Ce samples (Figure 8b2,c2, respectively), both of their \( |Z|_{0.01\text{Hz}} \) values at 0 h were almost equivalent to the nonscratched coatings. The Nyquist plots of their EIS spectra in Figure 9b,c also confirmed full recovery of the scratched area and almost completely overlapped with the nonscratched coatings’ spectra. However, the \( |Z|_{0.01\text{Hz}} \) value of SME-PCL5Ce (2.07E10 Ω) was higher than that of SME-PCL0Ce (1.27E10 Ω) because of the self-healing property of Ce(NO₃)₃. The high \( |Z|_{0.01\text{Hz}} \) values of SME-PCL5Ce indicated better corrosion resistance. This result correlated to the SEM image shown in Figure 6c2, which showed that the closure was sealed and completely healed. However, the increased immersion time reduced the impedance value of all coating systems because of degradation of the coating at the scratched area.⁹

In general, SME-PCL5Ce exhibited higher \( |Z|_{0.01\text{Hz}} \) values than those of SME-PCL0Ce and pure SME coatings, as shown in Figure 10. It was observed to increase impedance more than any of the other tested coating materials for all immersion durations.

**4. CONCLUSIONS**

The synthesis of self-healing PCL microspheres containing 5% Ce(NO₃)₃ (PCL5Ce) having an average size of less than 10 μm was successfully conducted. This was accomplished under a stirring condition of 1000 rpm for 10 h at 50 °C. Smaller particles were observed to be more effective in improving the self-healing property because they were able to contain higher amounts of Ce(NO₃)₃ per weight.

The self-healing property was improved by adding 10 wt % PCL5Ce to the SME (SME-PCL5Ce). In addition, the aluminum 2024-T3 plate was coated with the SME-PCL5Ce and heated at a healing temperature of 80 °C for 30 min to produce a good healing property. SEM images showed that the scratch width was completely healed and confirmed that the SME-PCL5Ce coating was able to repair the damaged coating.

![Figure 8a](https://example.com/fig8a.png)

**Figure 8a**. Bode plots of SME coated on aluminum 2024-T3 plates with scratching after heating (AH) at 80 °C for 30 min: (a) pure SME-AH, (b) SME-PCL0Ce-AH, and (c) SME-PCL5Ce-AH.

![Figure 8b](https://example.com/fig8b.png)

**Figure 8b**. Nyquist plots of SME coated on aluminum 2024-T3 plates with scratching after heating (AH) at 80 °C for 30 min: (a) pure SME-AH, (b) SME-PCL0Ce-AH, and (c) SME-PCL5Ce-AH.

![Figure 8c](https://example.com/fig8c.png)

**Figure 8c**. Nyquist plots of SME coated on aluminum 2024-T3 plates with scratching after heating (AH) at 80 °C for 30 min: (a) pure SME-AH, (b) SME-PCL0Ce-AH, and (c) SME-PCL5Ce-AH.

![Figure 9](https://example.com/fig9.png)

**Figure 9**. Nyquist plots of SME coated on aluminum 2024-T3 plates with scratching after heating (AH) at 80 °C for 30 min: (a) pure SME-AH, (b) SME-PCL0Ce-AH, and (c) SME-PCL5Ce-AH.

![Figure 10](https://example.com/fig10.png)

**Figure 10**. Correlation results between impedance and immersion time for pure SME, SME-PCL0Ce, and SME-PCL5Ce with heating at 80 °C for 30 min.
via thermally assisted self-healing. The corrosion resistance was proven by EIS measurement. After heating the scratched coating, the impedance of the scratched area was high and close to that of the nonscratched coating. This indicated a similar performance as the nonscratched coating. The results from FIB–SEM showed that Ce(NO$_3$)$_3$ was released and completely filled the scratched area. The cerium content analysis results provided by SEM–EDX analysis support the FIB–SEM result, which indicated that the chemical composition of the scratched area was Ce(NO$_3$)$_3$. Therefore, all results provided evidence that the SME-PCLScCe coating is sufficient to use as an anticorrosion coating.

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