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Corrosion and Heat Treatment of Paint Coating Containing Battery Cathode Waste Material-Epoxy Resin in 3.5 wt% Sodium Chloride Solution

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This study investigates the effect of heat treatment at 25, 100, 350, and 500 °C on the durability of mild steel samples coated with an epoxy paint coating system with various weight percentages of cathode waste material (CWM) in 3.5 wt% sodium chloride (NaCl). The epoxy paint coating systems incorporated with 0 and 10 wt% of CWM and exposed at 100 °C possessed reasonable thermal stability and barrier protection after the corrosion test. The results indicated that these coatings can protect the substrate from severe corrosion for 720 h of electrolyte immersion. Moreover, the high epoxy cross-linking and excellent filler particle arrangement improved paint coating adhesion on the mild steel surface.

Keywords: Cathode waste materials; Paint coating; Corrosion; Epoxy resin

1. INTRODUCTION

Organic paint coatings are widely used to protect metals against corrosion in atmospheric conditions [1]. However, their thermal stability at high-temperature environments requires further study as the demand for thermal-resistant coating increases. Mathivanan et al. [2] reported that conventional organic coatings, such as epoxy coatings, fail when used at high temperatures. The breakdown of polymer chains within the epoxy resin result in cracks, delamination, blisters, and pore formation, thereby affecting the corrosion protection properties of thermal-resistant paint coatings.

Several studies have been conducted to improve the thermal stability of paint coatings. However, organic materials alone cannot be used for high-performance applications because of their limited properties. Consequently, the addition of fillers that can withstand high temperatures, such as carbon black [3], silicone [2, 4], and silica [5] is frequently employed into the epoxy paint system to overcome restraint. Ramesh et al. [4] and Mathivanan et al. [6] reported significant corrosion protection for mild steel coated with conductive epoxy resin composite filler and exposed at temperatures of up to 225 °C after immersion in NaCl solution.

Belardi et al. [7] reported on the widespread consumption of disposable zinc–carbon batteries, which covers about 90 % of the European market. Most of these spent batteries are dumped in landfills and pose serious environmental problems. One of the products of recycling zinc–carbon batteries is cathode waste material (CWM), which contains carbon (C) element and can be used as a filler to improve the thermal properties of paint coatings.

Heat treatment on epoxy coating at various temperatures was examined in this study. The effect of corrosion on heat treatment was also evaluated by open circuit potential (OCP) analysis for mild steel samples coated with CWM–epoxy resin system exposed to 3.5 wt% NaCl solution. Moreover, morphological analysis was performed to support the findings.

2. EXPERIMENTAL

2.1. Preparation of CWM–epoxy resin paint

CWM particles were prepared using spent zinc–carbon battery from Eveready Battery Co., Inc. The cathode material was removed, rinsed with deionized water, and dried in a dry box. Milling was performed using a ball mill to reduce the particle size. Four batches of paints with varying CWM volume concentrations from 0 to 25 wt% were then prepared and abbreviated as 0, 10, 20, and 25 wt%. A paint binder was prepared by mixing the epoxy resin (DER 331, Euro Chemo-Pharma Sdn. Bhd.) with polyamide (A062, Euro Chemo-Pharma Sdn. Bhd.) in a 1:1 ratio. The procedure for CWM–epoxy paint preparation were discussed details in a previous study [8].

Thermogravimetric analyses (TGA) were conducted on the CWM–epoxy resin samples using a TGA machine (PerkinElmer PYRIS) at a heating rate of 10 °C min^{-1} under nitrogen atmosphere and at a temperature ranging from 30 to 600 °C.

2.2. Sample preparation

All systems were applied to the mild steel panels (industrial grade, 7 cm x 5 cm) by applying the doctor-blade technique. Coating thicknesses ranging from 40 to 60 μm were obtained. The samples were then cured in the laboratory at room temperature for 24 h. X-ray diffraction (XRD) was performed on the coating using a Bruker AXS D9 diffractometer to examine the various phases present.

2.3. Heat treatment

Heat resistance was applied according to the ASTM D-2485-91 guideline. The coated mild steel panels were treated at elevated temperatures ranging from 25 to 500 °C for 24 h using this standard. The morphology of the samples after heat treatment was examined by optical microscopy, and coating failure was then assessed.

2.4. Corrosion measurement

A polyvinyl chloride tube (7 cm long, 2 cm wide) was sealed to the mild steel panel surface with an epoxy after heat treatment, and the exposed coated area was fixed at 3.142 cm^2. The cell was then filled with 3.5 wt% NaCl solution and was left exposed to air. Change in potential with time after immersion was measured for 720 h (30 d) using a multimeter and a saturated calomel electrode (SCE) as reference electrode. A salt bridge was used to connect the 3.5 wt% NaCl solution and saturated potassium chloride electrolyte. Visual images of the immersed samples were recorded using an optical microscope.

3. RESULTS AND DISCUSSION

3.1. Characterization of raw materials

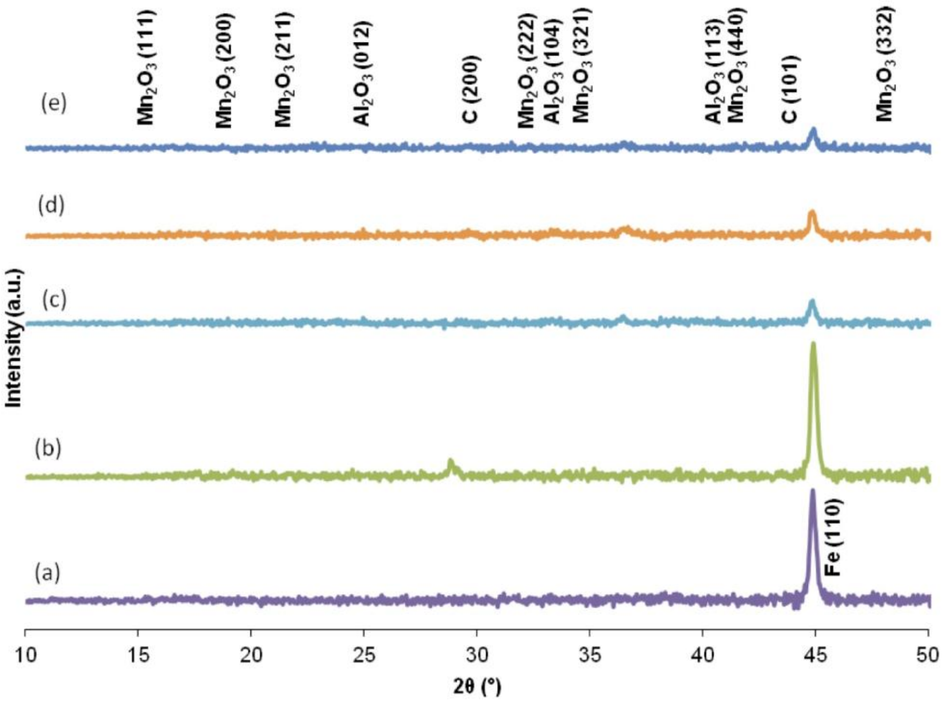


Figure 1. X-ray diffraction peaks of (a) bare mild steel and (b) 0, (c) 10, (d) 20, and (e) 25 wt% of CWM-epoxy resin systems.

Figure 1 shows the XRD peaks of the bare mild steel and mild steel samples coated with CWM-epoxy resin systems. The XRD pattern revealed the presence of Fe planes for the bare mild steel as well as for the sample coated with 0 wt% of CWM, which conforms to the main element of the substrate used (Figures 1a and 1b). Fe matched with ICDD file no. 00-006-0696 and the Fe peak was detected at 2θ = 44.67°, which corresponds to the (110) plane. Several new phases were observed after the application of thermal resistance paint coating, such as C (ICDD 01-075-1621), manganese (III) oxide (Mn_2O_3, ICDD 00-041-1442), and aluminum oxide (Al_2O_3, ICDD 00-046-1212), which correspond to the CWM contents in the paint coating (Figures 1c–1e).

All these elements are common CWM contents. MnO_2 is the main active material in the cathode for zinc–carbon battery, whereas carbon powder is mixed with MnO_2 to improve conductivity and ability to retain the electrolyte. McComsey et al. [9] stated that Zn is oxidized and MnO_2 is reduced when the cell is discharged. Thus, the existence of Mn_2O_3 and C were justified. Al_2O_3 comes from the impurities that may occur during the sample preparation. A simplified overall cell reaction can be expressed as follows:

$$Zn + 2MnO_2 + 2H_2O + ZnCl_2 \rightarrow Mn_2O_3.H_2O + 2Zn(OH)Cl \qquad (1)$$

3.2. Thermogravimetric analysis

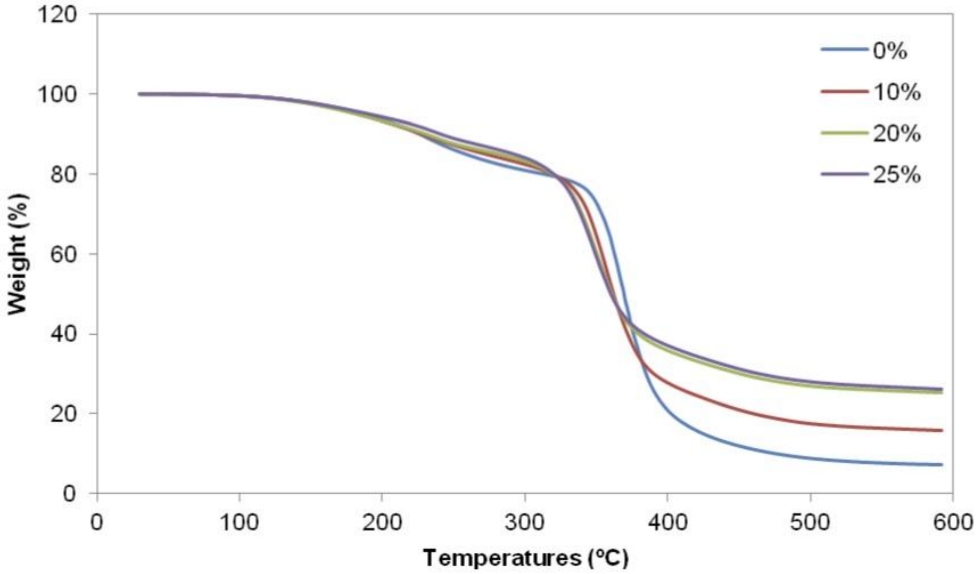


Figure 2. Thermogravimetric analysis for 0, 10, 20, and 25 wt% of CWM–epoxy resin systems.

Figure 2 shows the TGA of the CWM–epoxy resin paint systems. All batches exhibited almost similar trends, but resulted in various weight loss percentages at the end of the temperature curve. A minimal weight loss was recorded when temperature exceeded 150 °C. However, an abrupt weight loss in the epoxy resin was observed at high temperatures from approximately 300 to 450 °C. Full degradation of the epoxy resin occurred beyond 500 °C, leaving residues. More residues were obtained with the addition of CWM contents.

The initial weight loss at 150 °C may be attributed to the evaporation of trapped gas and volatile matter from the inner epoxy resin during the coating application [10]. Rapid weight loss due to the degradation of epoxy resin was observed at 300 °C. This result was in accordance with the report by Armelin et al. [11], which suggested that the cross-linking of epoxy resin was broken down and the epoxy resin physically cracks when the temperature reaches about 300 °C. The residues of the heat treatment at 600 °C consisted of C, which was not eliminated. Therefore, thermal behavior was not affected by the addition of CWM contents.

3.3. Heat treatment analysis

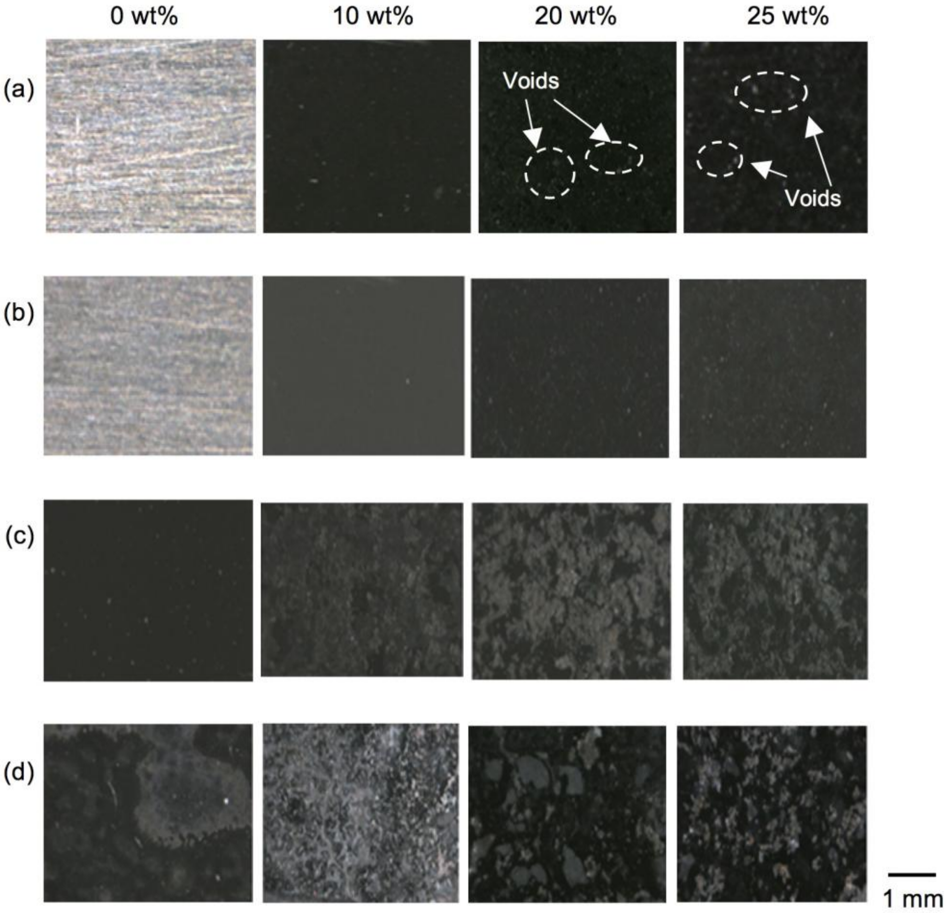


Figure 3. Morphologies of coated mild steel samples after heat treatment at (a) 25, (b) 100, (c) 350, and (d) 500 °C with 0, 10, 20, and 25 wt% of CWM fillers.

Figure 3 shows the morphologies of the coated mild steel samples after heat treatment at an elevated temperature ranging from 25 to 500 °C with different CWM filler contents. The morphology of the mild steel sample coated with 0 wt% of CWM and exposed at 25 °C (Figure 3a) was used as control sample. The 0 wt% of CWM-epoxy resin paint coating provided a transparent coating film, which turned to black with the addition of CWM. This change in color was attributed to the black carbon powder, which provided the color pigment in this paint coating system. Meanwhile, all CWM-epoxy resin systems adhered well to the mild steel surface after drying.

A small amount of CWM particles became visible at 10 wt% of CWM coating (Figure 3a), concomitant with the increased in surface roughness as the amount of filler was increased. Agglomerations of CWM particles and void formations were observed for samples containing 20 wt% onwards. Vilche et al. [12] reported that the high percentage of filler contributes to fast sedimentation and strong agglomeration of particles, which cannot be easily dispersed.

Interestingly, all mild steel samples coated with CWM-epoxy resin systems exhibited better surface morphology at 100 °C compared with the sample exposed at 25 °C (Figure 3b). Each coating system showed a smooth and fully cured surface, with no sign of corrosion spots, indicating that the CWM particles were well dispersed on the epoxy binder. At 100 °C , the expansion of epoxy resin reopened the passages for the diffusion of CWM particles into the epoxy coating layer as the melting point of epoxy resin is 105 °C. El-Tantawy et al. [3] also reported improvement in the network structure of the epoxy matrix with the addition of C filler.

An obvious change was observed after the mild steel samples coated with CWM-epoxy resin system were exposed at 350 and 500 °C, as shown in Figures 3c and 3d, respectively. The epoxy coating with 0 wt% of CWM formulation was degraded, leaving polymer ashes on the mild steel. Similar behavior was observed in the mild steel sample coated with 10 to 25 wt% of CWM when the paint system can no longer protect the mild steel panel because of severe chalking and delamination. Each system appeared to have decomposed at this temperature, consistent with the result reported by Jimenez et al. [13].

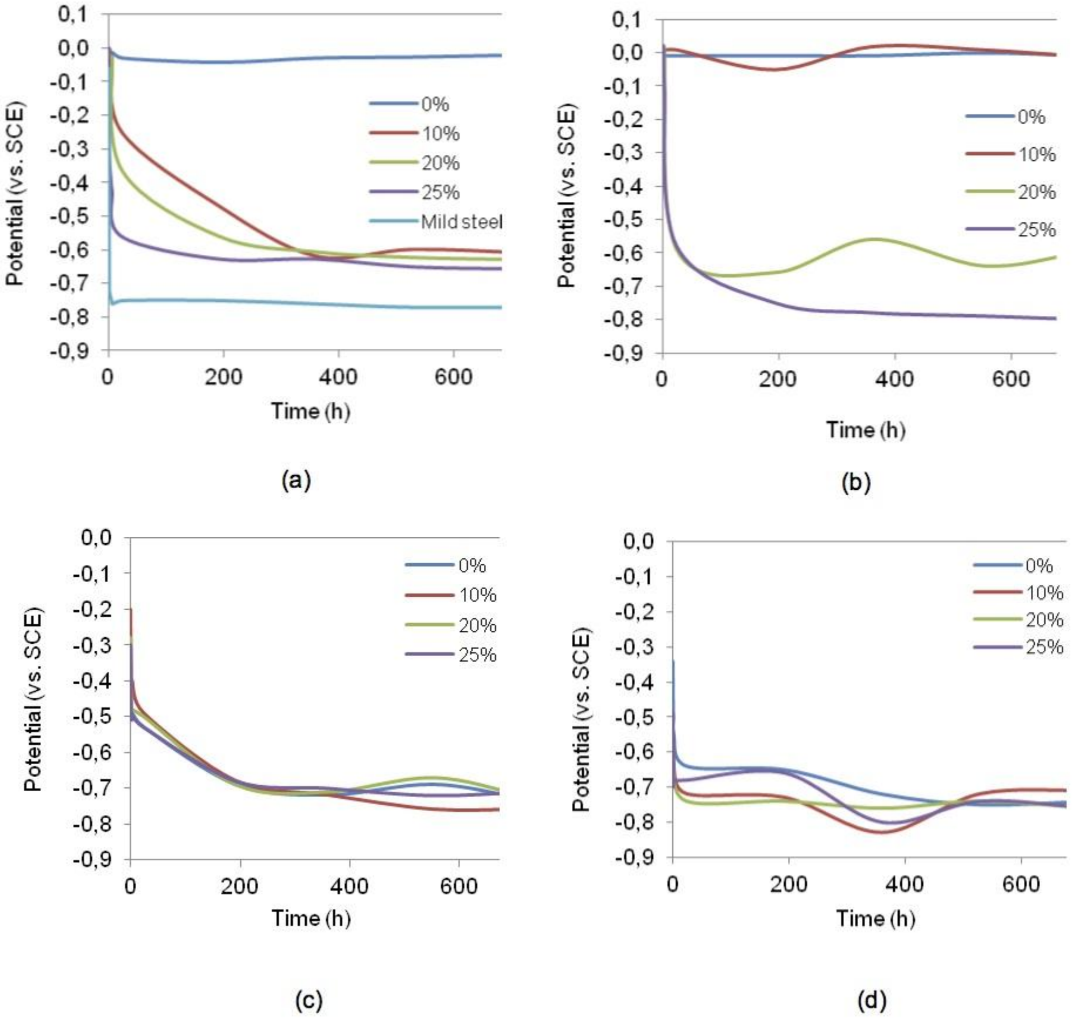
This finding was also in accordance with the TGA result, which depicted the change in weight loss when temperature achieved >300 °C. Meanwhile, Miszczyk et al. [1] revealed that the changes in temperature affected the coated metal by changing the mechanical properties of the visco-elastic coating. Consequently, microcracks on the coating surface occured, as well as delamination from the mild steel substrate.

3.4. Open circuit potential analysis

Figure 4 presents the OCP characteristic of bare mild steel and mild steel samples coated with CWM-epoxy resin system at different heat treatments in 3.5 wt% NaCl solution. The results showed that the control sample of bare mild steel reached corrosion potentials of -0.75 V (vs. SCE) immediately after immersion (Figure 4a). Hence, mild steel was considered corroded until the end of the immersion. This result was similar to that reported in the study by Martyak et al. [14], in which chloride ion corrodes bare mild steel rapidly at a mild steel corrosion potential of -0.60 V (vs. normal hydrogen electrode) and a pH of 7.0.

The OCP for the mild steel coated with 0 wt% of CWM was stable at 0.0 V (vs. SCE) during the entire immersion. This potential value indicates that no ion exchange occurred and that the barrier coating was successfully implemented. A steep drop in potential value occurred immediately after immersion for t = 48 h for the paint coating incorporated with 10, 20, and 25 wt% of CWM (Figure 4a). The potential continued to decrease at a lower rate until after 720 h to potential values below -0.60

V (vs. SCE). In addition, the increase in CWM fillers in the epoxy coating resulted in a higher OCP reduction rate of the coated mild steel samples.



(a)

(b)

(c)

(d)

Figure 4. Open-circuit potential characteristics of mild steel samples coated with 0, 10, 20, and 25 wt% of CWM-epoxy resin systems after heat treatment at (a) 25, (b) 100, (c) 350, and (d) 500 °C in 3.5 wt% NaCl solution.

Evidently, the mild steel sample coated with 0 wt% of CWM-epoxy resin coating system exposed at 100 °C exhibited superior protective performance compared with the other coating compositions (Figure 4b). The potential of this sample remained at c. a. 0.0 V. Comparable OCP result of the mild steel sample coated with 10 wt% of CWM-epoxy resin coating system exposed at 100 °C exhibited a slight fluctuation until after 720 h of immersion. The high epoxy cross-linking and excellent filler particle arrangement within the paint coating layer during the heat treatment helped maintain the potential value. However, the potential for mild steel samples incorporated with 20 and 25 wt% of CWM exposed at 100 °C temperature dropped rapidly within 24 h of immersion and continued to decrease until the end of immersion time to reach potential values below -0.60 and -0.80 V (vs. SCE), respectively.

Meanwhile, the potential of all mild steel samples coated with CWM-epoxy resin system after heat treatment at 350 and 500 °C dropped immediately and continued to decrease to the corrosion potential of the bare mild steel (Figures 4c and 4d). This behavior indicates that these coated paints were degraded with time and failed to provide a protective barrier on the mild steel samples. This result was in accordance with that in other studies [1], in which the adhesive bond strength was diminished because of coating degradation, thereby creating pathways for electrolyte penetration to reach the steel surface within short exposure times.

3.5. Morphological analysis

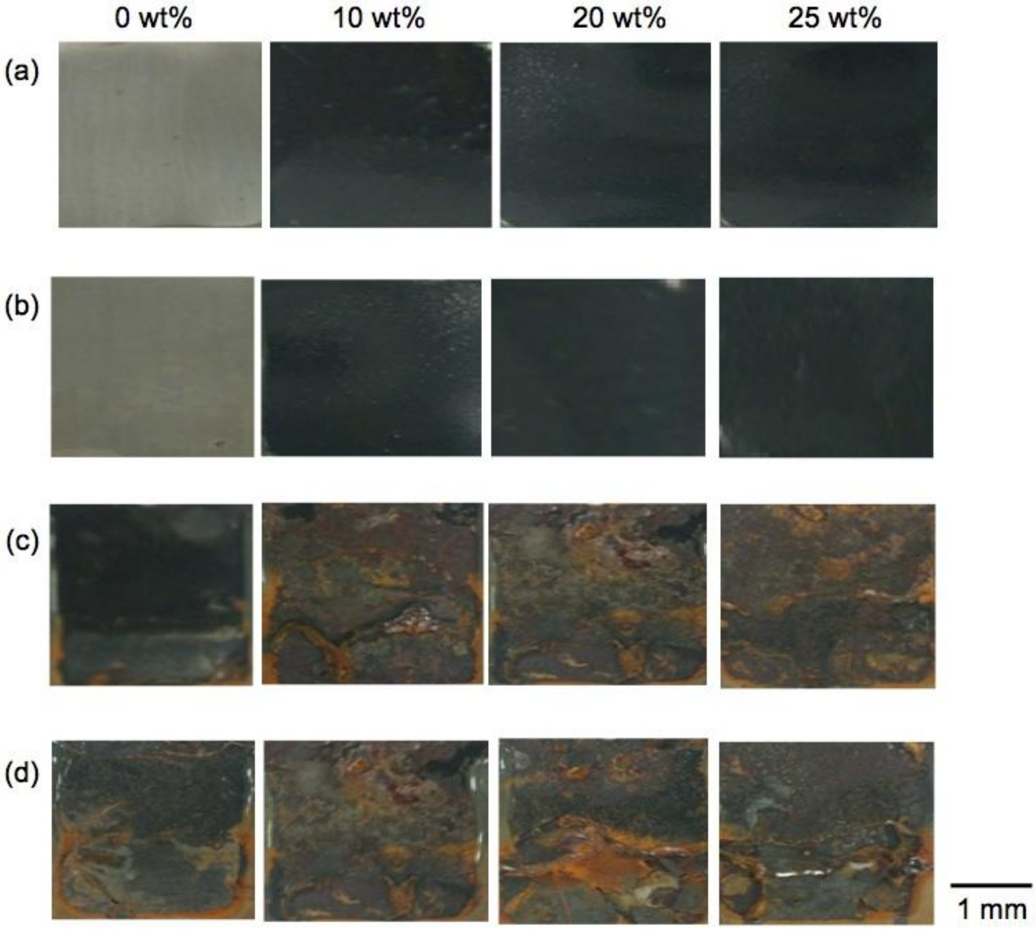


Figure 5. Morphologies of the mild steel samples coated with 0, 10, 20, and 25 wt% of CWM-epoxy resin systems exposed at (a) 25, (b) 100, (c) 350, and (d) 500 °C after OCP measurements in 3.5 wt% NaCl solution, respectively.

Figure 5 shows the morphologies of the mild steel samples coated with CWM-epoxy resin system after the OCP analysis with respect to their heat treatments. Visual examination on the coated samples exposed at 25 and 100 °C demonstrates no observable changes after the OCP measurements (Figures 5a and 5b). Despite the result, orange/brownish colored corrosion products were evident on the paint system exposed at 350 and 500 °C after immersion in the corrosive electrolyte for 720 h (Figures 5c and 5d). This corrosion product developed crack lines that totally uncovered the mild steel. Iron dissolution occurred, whereas water and oxygen gas were reduced on the mild steel surface during this contact. Hence, the rapid ion exchange was unblocked, and the mild steel was covered with the corrosion product because of the formation of an oxide layer.

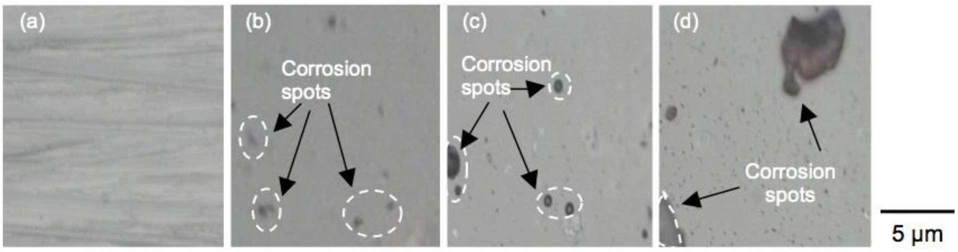


Figure 6. Mild steel samples coated with (a) 0, (b) 10, (c) 20, and (d) 25 wt% of CWM–epoxy resin systems exposed at 25 °C after OCP measurement in 3.5 wt% NaCl solution.

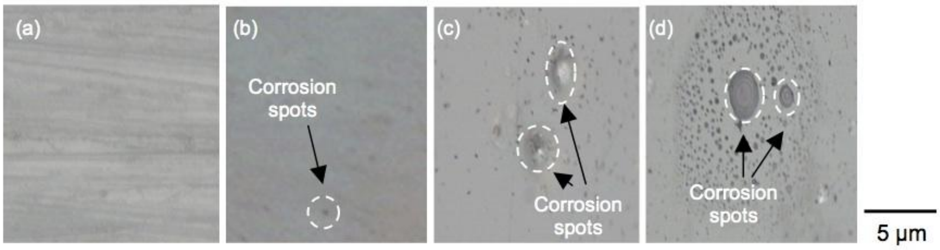


Figure 7. Mild steel samples coated with (a) 0, (b) 10, (c) 20 and (d) 25 wt% of CWM–epoxy resin systems exposed at 100 °C after the OCP measurement in 3.5 wt% NaCl solution.

Further optical magnification shows no obvious changes for samples incorporated with 0 wt% of CWM after heat treatment at 25 °C, with no signs of corrosion or electrolyte penetration even after 720 h of immersion in 3.5 wt% NaCl electrolyte (Figure 6a). However, several localized corrosion spots were revealed for samples coated with 10, 20, and 25 wt% of CWM (Figures 6b–6d), which was consistent with the results of the OCP measurements. Figure 7 shows a similar behavior for mild steel samples coated with 0 wt% of CWM after heat treatment at 100 °C, with no evidence of corrosion products.

A number of localized corrosion spots were observed for samples incorporated with 10 wt% of CWM, where corrosion was initiated. Samples coated with 10 wt% of CWM after heat treatment at 100 °C provided better barrier properties that promoted the adhesion of epoxy resin to the metal substrate, thereby improving resistance against corrosion compared with the sample coated with the same filler contents after heat treatment at 25 °C. Severe corrosion spots were observed for samples with higher CWM loadings (Figures 7c and 7d), where more corrosion products are visible.

The increases in CWM content resulted in the growth of corrosion activities because of the high porosity behavior of carbon as the main element in the CWM compound, which provided a large surface area for electrolyte adsorption [8, 9]. Therefore, more electrolytes penetrated the polymeric barrier and came into contact with the steel surface, causing mild steel corrosion. Hence, the growth of corrosion products led to cracks and delamination of the coating layer [11].

4. CONCLUSIONS

Heat treatment exhibited a significant effect on the protective properties of mild steel samples coated with CWM-epoxy resin system. The corrosion result proved that the addition of 10 wt% of CWM filler resulted in satisfactory barrier protection in the coated paint system as well as with the sample coated with 0 wt% of CWM after heat treatment at 100 °C. This paint coating system produced a smooth and highly cured surface because of the better adhesion provided by the epoxy resin and the thermal resistance behavior of the combined CWM particles in the coating system. However, a further increase in temperature caused the degradation of CWM-epoxy resin paint coatings, thereby contributing to failures, such as blisters, voids, cracks, chalking, and delamination of the coated film. Meanwhile, the addition of CWM contents to the epoxy resin paint system only led to agglomeration and formation of voids; thus reducing corrosion resistance.

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