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Corrosion Studies of Conductive Paint Coating Using Battery Cathode Waste Material in Sodium Chloride Solution

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A conductive paint coating was prepared using a mixture of cathode waste materials (CWM) as the filler and epoxy resin as the binder. The optimum electrical conductivity of 5.33 × 10^{-4} S cm^{-1} was obtained at 25 wt% CWM. It was found that the contact of the filler improves the electrical conductivity. However, the corrosion potential (E_{corr}) values of paint/mild steel decreased with the higher percentage of CWM to the paint. The low percentage incorporation of the filler shows the best ability to protect the mild steel from corrosion among the coatings.

Keywords: Cathode waste materials; Conductive paint coating; Corrosion; Epoxy resin.

1. INTRODUCTION

Paint coating is regarded as one of the most economical and widely used methods of protecting metal. The coating layer acts as a barrier that isolates the metal from the corrosive environment that causes deterioration of material. Thus, the coating layer enhances the lifetime of the metal [1]. Epoxy resins are one of the most well-known binders that are used for a wide variety of protective coatings because of their excellent adhesion, good mechanical properties, and tremendous corrosion resistance performance [2]. At the same time, pigments are added to give extra characteristics to meet special requirements for various new applications [3, 4].

Conductive paint is a type of paint coating that is produced by adding various types of electrical conducting materials into the binder such as metal [3], carbon black [5, 6], graphite [7, 8], conductive polymers [2, 8-10] and carbon fibres [11, 12]. By being conductive, the paint can be used as an antistatic agent to reduce or eliminate the buildup of static charges. The static charges could cause damage to static-sensitive objects such as electronic devices and might produce sparks that would ignite flammable gasses or liquid [3, 5, 8, 9]. Various corrosion studies have been performed on conductive paint coating. Significant corrosion protection was reportedly obtained by Armelin et al. [2] and Masri et al. [5] for samples coated with conducting polymer in sodium chloride (NaCl) solution.

Freitas et al. [13] found that the growing disposal of spent zinc-carbon batteries has created a serious environmental problem. This kind of battery consists of various materials that decompose and deteriorate with difficulty, and thus finally leach out and contribute to landfill. Nevertheless, zinc-carbon batteries can be recycled since one of the materials, the cathode waste material (CWM), can be used as a conductive filler in paint coating due to the conductive behaviour of the carbon (C) element in the CWM. As a result, the disposal of zinc-carbon batteries will be reduced.

In this work, the electrical conductivity of epoxy coating with different weight percentages of CWM was studied. Besides that, corrosion testing was conducted to gain further understanding of the effect of corrosion protection ability for mild steel coated with an epoxy resin–CWM system when exposed to 3.5 wt% NaCl solution. Morphological, elemental, and phase analyses are also implemented to support the findings.

2. EXPERIMENTAL

2.1 Preparation of conductive paint

CWM particles were prepared using typical spent zinc-carbon batteries from Eveready Company. The cathode material was taken out, rinsed with deionized water, and dried in a dry box. A milling process was carried out using a ball mill to reduce the particle size. Then, a sieving process was performed to collect particles with sizes smaller than 5 µm. After that, energy dispersive spectroscopy (EDX, Zeiss Supra^{TM}, 35VP) analysis was performed to identify the elements that existed in the CWM.

A series of paints with different CWM contents were prepared. The paint binder was prepared by mixing the epoxy resin (DER 331, Euro Chemo-Pharma Sdn. Bhd.) with polyamide (A062, Euro Chemo-Pharma Sdn. Bhd.) at a ratio of 1:1. The percentage of CWM particles was calculated using Eqn. (1):

$$\mathrm{CWM}(\%) = \frac{\text{Mass of CWM}}{\text{Mass of epoxy resin} + \text{Mass of polyamide} + \text{Mass of CWM}} \times 100\% \qquad (1)$$

2.2 Sample preparation

Mild steel panel (industrial grade) was used as the substrates. The surface of the mild steel was ground and polished by using a common metallographic technique. The mild steel panel was then cleaned and dried. The mild steel panels, 8 × 5 cm^2 in size, were covered with conductive paint coating at different CWM percentages by using the doctor's blade technique. Coating thicknesses of approximately 50 μm were obtained. The paints were dried in the laboratory at room temperature for 24 hours. Field emission scanning electron microscopy (FESEM, Zeiss Supra^{TM}, 35VP) and optical microscopy (Olympus, BX51M) were used to characterize the morphologies of these samples.

2.3 Conductivity measurement

The conductivity of the conductive paint was measured using an ADVANTEST R8340 ultra high resistance meter (Japan). The relationship of conductivity is as follows:

$$\sigma = \frac{J}{E} \tag{2}$$

where σ is the conductivity, *J* is the current density (A cm^{-2}), and *E* is the intensity of electric strength. The conductivity is equal to the slope in the plot of *J* versus *E*.

2.4 Corrosion measurement

A polyvinyl chloride (PVC) tube (7 cm long, 2 cm diameter) was sealed onto the painted surface by means of epoxy glue and the exposed coated area was fixed at 3.142 cm^2. The cell was then filled with 3.5 wt% NaCl solution and left open to the air. The open circuit potential (OCP) was measured for 30 days using a voltmeter and saturated calomel electrode (SCE) as the reference electrode. A salt bridge was used to connect the 3.5 wt% NaCl with the saturated potassium chloride (KCl) electrolyte.

After finishing, the visible exposed area of the investigated coating samples and the cross-section images were recorded via optical microscope. In addition, X-ray diffraction (XRD, Bruker AXS D9) was performed on the coating samples before and after their exposure to 3.5 wt% NaCl to identify any phase changes in the samples.

3. RESULTS AND DISCUSSION

3.1 Energy Dispersive Spectroscopy analysis

The results of the Energy Dispersive Spectroscopy (EDX) analysis of CWM particles are listed in Table 1. C has the highest content (39.00 wt%), followed by manganese (Mn, 19.74 wt%), oxygen (O, 13.86 wt%), and zinc (Zn, 12.83 wt%). All of these elements are common contents of CWM, while the other elements are additive to the battery.

Generally, manganese dioxide (MnO_2) is the main active material in the cathode of zinc-carbon batteries while C is mixed with the MnO_2 in order to improve the conductivity as well as to increase the ability to retain the electrolyte. Thus, the existence of Mn, O, and C was justified. The presence of Zn in the CWM contributed to the dissolution of the Zn anode during the discharge process. According to McComsey et al. [14], when the cell is discharged, the Zn will be oxidized while the MnO_2 will be reduced. The reaction can be written as follows:

$$Zn + 2MnO_2 + 2H_2O + ZnCl_2 \rightarrow Mn_2O_3.H_2O + 2Zn(OH)Cl \qquad (3)$$

Table 1. Elemental percentages of CWM.

Element	Weight percentage (%)
C	39.00
O	13.86
Na	5.56
Al	0.71
Si	1.48
Cl	5.71
Ca	1.11
Mn	19.74
Zn	12.83

3.2 Electrical conductivity analysis

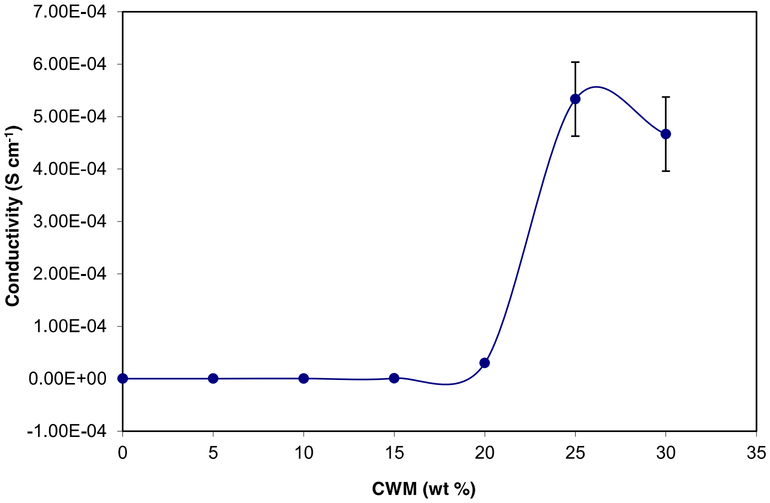

Figure 1. Electrical conductivity of epoxy coating as a function of different weight percentages of CWM.

The electrical conductivity result for the conductive paint coating at different percentages of CWM is shown in Fig. 1. At low filler content (<20 wt% of CWM), the coatings behave like a pure insulator as the conductivity obtained was close to zero. With the addition of 20 wt% CWM, a small increment of electrical conductivity was recorded at 3.0×10^{-5} S cm^{-1}. A steep increase in conductivity was observed when the CWM content exceeded 20 wt%. The maximum conductivity of 5.33×10^{-4} S cm^{-1} was seen at 25 wt% CWM. However, beyond this critical value, the conductivity level showed a slight decrease to 4.67×10^{-4} S cm^{-1} with the addition of 30 wt% CWM.

The maximum conductivity value achieved at 25 wt% CWM was consistent with the work done by Tsotra et al. [12], who obtained an electrical conductivity of the order of 10^{-4} S cm^{-1} with the addition of carbon fibre as the conductive pigment. Besides that, Masri et al. [5] also achieved a maximum value of conductivity in the range of 10^{-4} S cm^{-1} with the addition of 20 wt% carbon black additive. This indicates that CWM acts successfully as filler and improves the electrical conductivity at the optimum weight percentage of 25 wt% CWM, which is comparable with other conductive filler filled polymers.

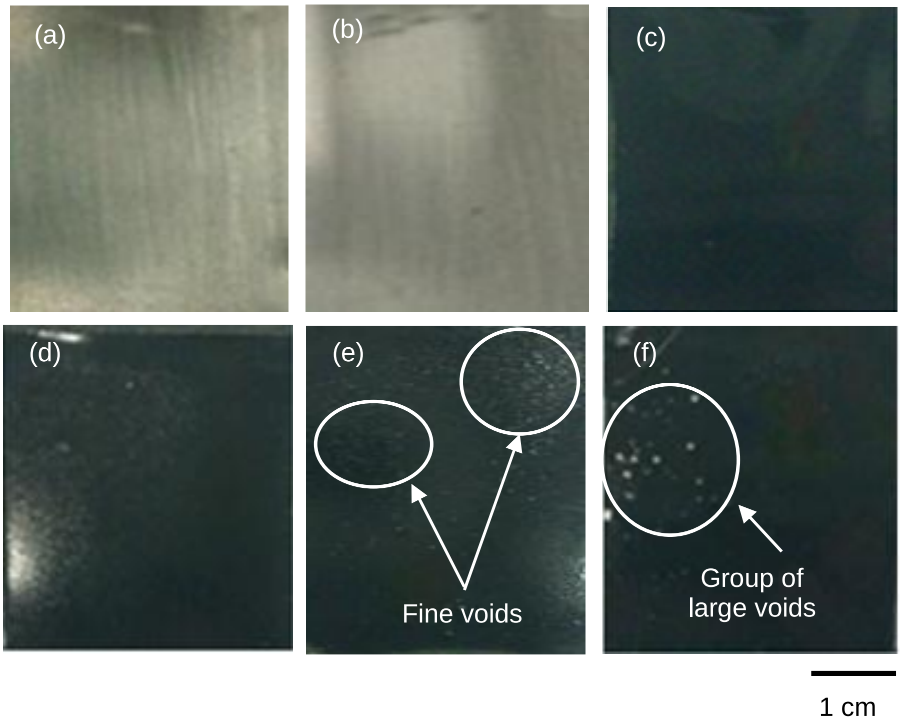

Figure 2. Image of (a) bare mild steel, (b) plain epoxy, (c) 10, (d) 20, (e) 25, and (f) 30 wt% CWM–epoxy resin conductive coating after drying at room temperature for 24 hours.

Figure 2 shows images of the samples after they were dried at room temperature for 24 hours. Figures 2a and 2b show the surfaces of bare mild steel and mild steel coated with plain epoxy, which were used as the control samples, respectively. Meanwhile, all CWM–epoxy paint coatings were adhered well to the mild steel surface after the drying process (Figs. 2c–2f). Furthermore, it is noted that CWM–epoxy resin coating systems provide proper conditions to act as protective coating.

However, the surface roughness of the paint was affected by the increase in the amount of filler. The agglomeration of CWM became obvious starting from the composition of 25 and 30 wt% CWM (Figs. 2e and 2f). In addition, this problem also caused difficulties while spreading the paint evenly on top of the mild steel substrate and also contributed to the formation of bubbles. Thus, 30 wt% CWM was the maximum amount used in this work.

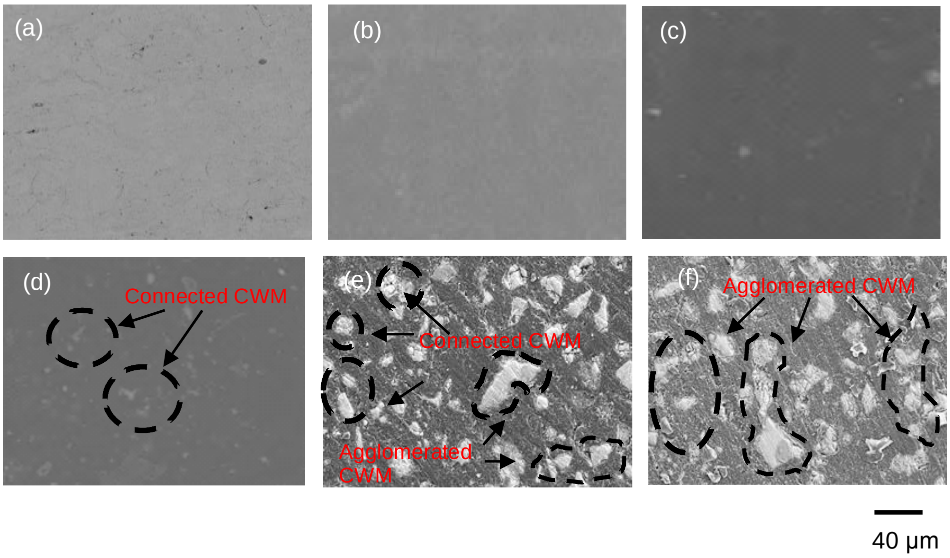

Figure 3. FESEM morphology of polished surface CWM–epoxy resin coating for (a) bare mild steel, (b) plain epoxy, (c) 10, (d) 20, (e) 25, and (f) 30 wt% CWM.

Figure 3 shows the FESEM morphologies of the bare mild steel, plain epoxy coating and conductive paint coatings with different percentages of CWM. The morphologies of the bare mild steel (Fig. 3a) and mild steel coated with plain epoxy (Fig. 3b) were used as controls. With 10 wt% CWM coating (Fig. 3c), small amounts of CWM start to become visible. Nevertheless, the filler particles in this paint are hardly connected with each other.

Different results are observed as the amount of filler increases to 20 and 25 wt% (Figs. 3d and 3e). With this composition, CWM starts to form a network between the filler particles although agglomerations begin to be seen at 25 wt% CWM. As shown in Fig. 3f, the presence of large agglomerates of CWM on the mild steel surface is clearly observed and heterogeneous films are produced since the dispersion is uneven. On the other hand, Vilche et al. [15] revealed that the high percentage of filler contributes to a fast sedimentation and strong agglomeration of particles which cannot be easily dispersed.

It can be seen that the difference in conductive behaviour corresponds to the enhanced number of conductive paths in the paint coating. When the content of CWM particles in the coating is relatively low (0–20 wt%), the conducting filler particles are not attached to each other, which makes the movement of electrons difficult. As a result, a lower conductivity is achieved. Johnson et al. [11] suggested that the content of filler particles must be high enough to allow the conductive particles to make contact with each other or to be sufficiently close to permit tunnelling through a thin layer of insulating polymer matrix to form a complete electrical path.

The maximum conductivity will be obtained when enough CWM particles (25 wt% CWM) are in contact with each other and form a network for electron movement. Zheng et al. [8] found that the electrical conductivity of the composites exhibited a pronounced transition with the increase of filler content from an insulator to nearly a semiconductor with the optimum addition of filler. Dispersion of CWM on the mild steel surface is also important to determine the variation in the percolation threshold for the conductivity transition [7]. Based on the measurements performed, it is possible to state that coating containing about 25 wt% CWM exhibits satisfactory electrical conductivity properties.

3.3 Open circuit potential analysis

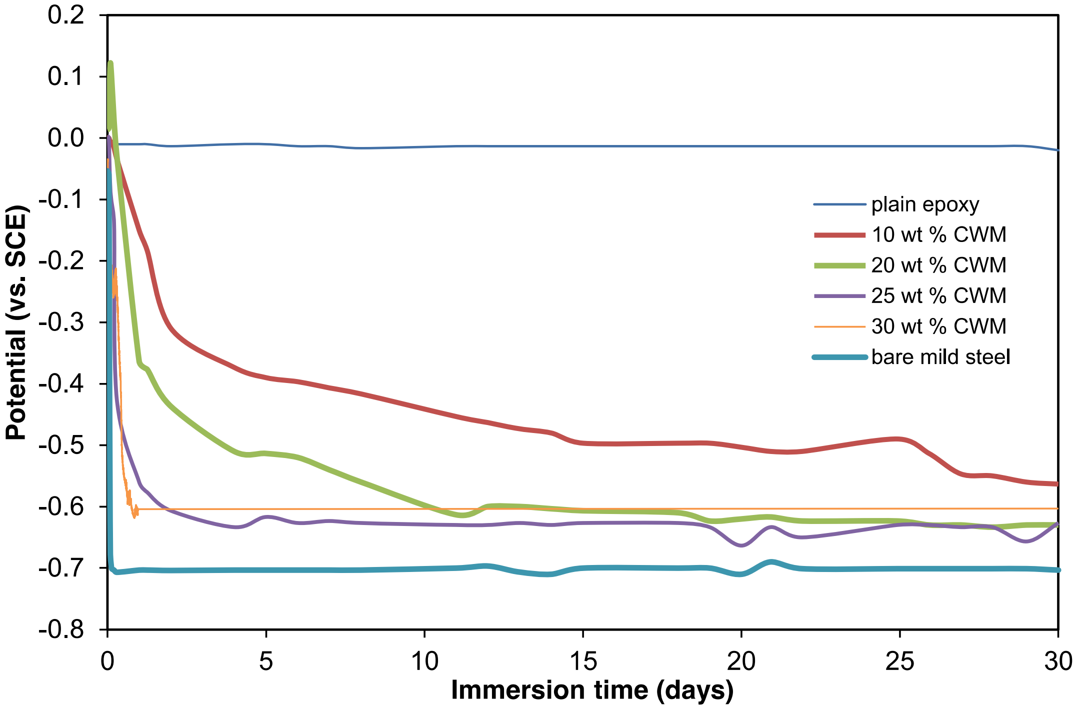

Figure 4. OCP plots of bare mild steel coated with CWM-epoxy resin after immersed for 30 days in 3.5 wt% NaCl solution.

Figure 4 shows the OCP characteristics of bare mild steel and the CWM-epoxy resin system in 3.5 wt% NaCl electrolyte. The results show that the control sample of bare mild steel reaches corrosion potentials of –0.703 V (vs. SCE) immediately after immersion. From this point onwards, the mild steel was considered as corroded until the end of the immersion test. This result is similar to that reported by Martyak et al. [9], who stated that chloride medium corrodes bare mild steel rapidly at a mild steel corrosion potential (E_{corr}) of –0.60 V (vs. NHE) and pH of 7.0. On the other hand, the OCP for the mild steel coated with plain epoxy was stabilized at 0.0 V (vs. SCE). This potential value indicates full protection of steel from any reaction.

A steep drop in potential can be seen from the beginning of immersion for two days of immersion for conductive paint coating incorporating 10 wt% CWM. The potential continues to drop but at a lower rate after the end of the steep region. Interestingly, the potential reached only –0.56 V (vs. SCE) after 30 days of immersion. Similar trends are observed on the mild steel sample coated with 20, 25, and 30 wt% CWM, for which the potentials drop rapidly within one day of immersion and continue to decrease at a lower rate until the end of the immersion time, reaching values below –0.60 V (vs. SCE).

It is noticeable that at the higher percentages of CWM content, the measured electrode potential values drop quickly to reach the E_{corr} of bare mild steel. At this stage, only the 10 wt% CWM–epoxy resin system coating formulation was able to protect the mild steel for approximately 30 days compared to the other CWM–epoxy resin systems. This shows that the penetration of the corrosive ions into this coating system is minimal at 10 wt% CWM. As the main element in the CWM compound, carbon is known to be porous and to possess a large surface area that is available for adsorption of electrolyte [14]. Therefore, as the CWM particles increase, the conductive paint coating tends to have higher porosity. Hence more electrolyte will penetrate the polymeric barrier and come into contact with the steel surface, causing the mild steel to be corroded. A similar result has been reported by Marchebois et al. [6], who found that when an increase in porosity is induced by the addition of carbon black, it resulted in rapid penetration of electrolyte toward the substrate.

3.4 Morphological analysis

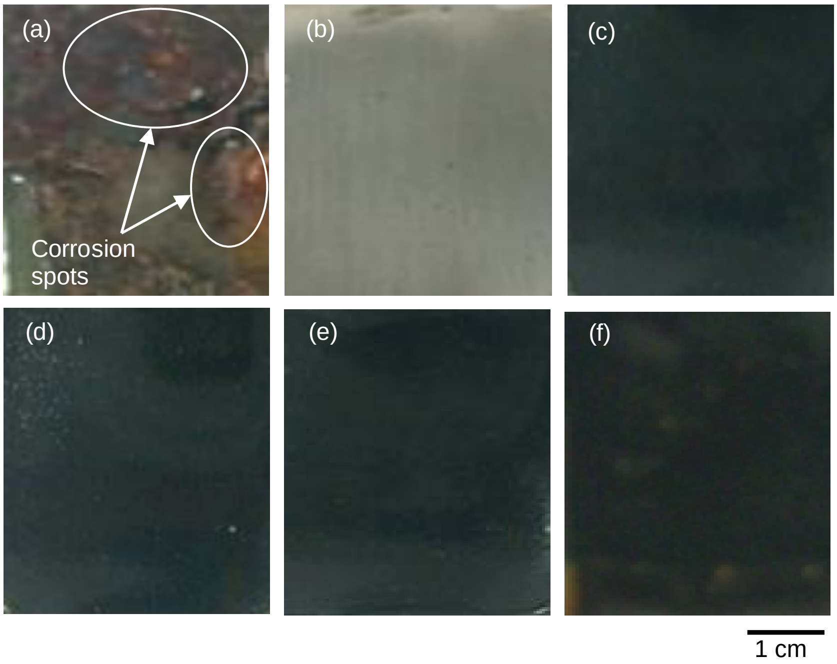

Figure 5. Image of (a) bare mild steel, (b) plain epoxy, (c) 10, (d) 20, (e) 25, and (f) 30 wt% CWM–epoxy resin conductive coating after exposure to 3.5 wt% NaCl solution in the OCP analysis.

Figure 5 shows an image of the samples after they were exposed to 3.5 wt% NaCl solution in the OCP analysis. Corrosion was evident for the bare mild steel sample after it was immersed for 30 days in a corrosive environment (Fig. 5a). However, the surfaces of the mild steel with plain epoxy coating and with 10 wt% CWM coating do not experience any changes, with no sign of corrosion being observed after the immersion (Figs. 5b and 5c). For the mild steel sample coated with 20, 25, and 30 wt% CWM, the changes were hardly noticeable by the naked eye (Figs. 5d–5f). To observe this area in greater detail, cross-sectional images of every sample after exposure to 3.5 wt% NaCl solution were taken for further analysis.

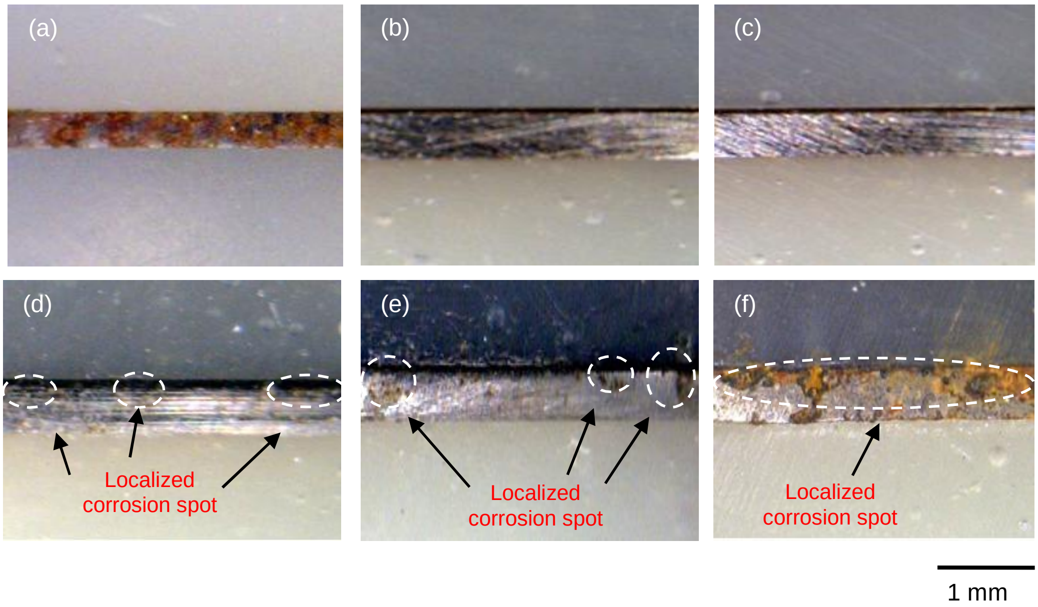

Figure 6. Cross-section image of (a) bare mild steel, (b) plain epoxy, (c) 10, (d) 20, (e) 25 and (f) 30 wt% CWM–epoxy resin conductive coating after exposure to 3.5 wt% NaCl solution in the OCP analysis.

The orange/brownish coloured corrosion products were present at the cross-sectioned surface of the bare mild steel sample (Fig. 6a). As expected, no changes were detected at the surfaces of mild steel coated with plain epoxy and with 10 wt% CWM (Figs. 6b and 6c). However, a very small number of localized corrosion spots were recognized on the sample of mild steel coated with 20 wt% CWM (Fig. 6d). The results deteriorated for samples with higher CWM loadings (Figs. 6e and 6f), on which more localized corrosion spots were observed. In addition, a mixture of black and brown coloured corrosion products was obtained at the interface of the coating with the mild steel and is believed to be Fe_3O_4 and Fe_2O_3. Besides that, Masri et al. [5] also reported changes in the colour of a mild steel sample after exposure to a corrosive environment.

3.5 Elemental and phase analysis

Figure 7 shows the XRD peaks of bare mild steel and samples coated with the CWM–epoxy resin system before their exposure to 3.5 wt% NaCl solution in the OCP analysis. The XRD pattern initially revealed the presence of Fe planes for bare mild steel and for the sample coated with plain epoxy conforming to the main element of substrate used (Figs. 11a and 11b). Fe is matched with ICDD file no. 00-006-0696 and the Fe peaks are detected at $2\theta = 65.02$, and 82.33°, which correspond to the 200, and 211 planes, respectively. Several new phases are observed after the application of conductive 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 corresponds to the CWM content in the conductive paint coating (Figs. 7c–7f).

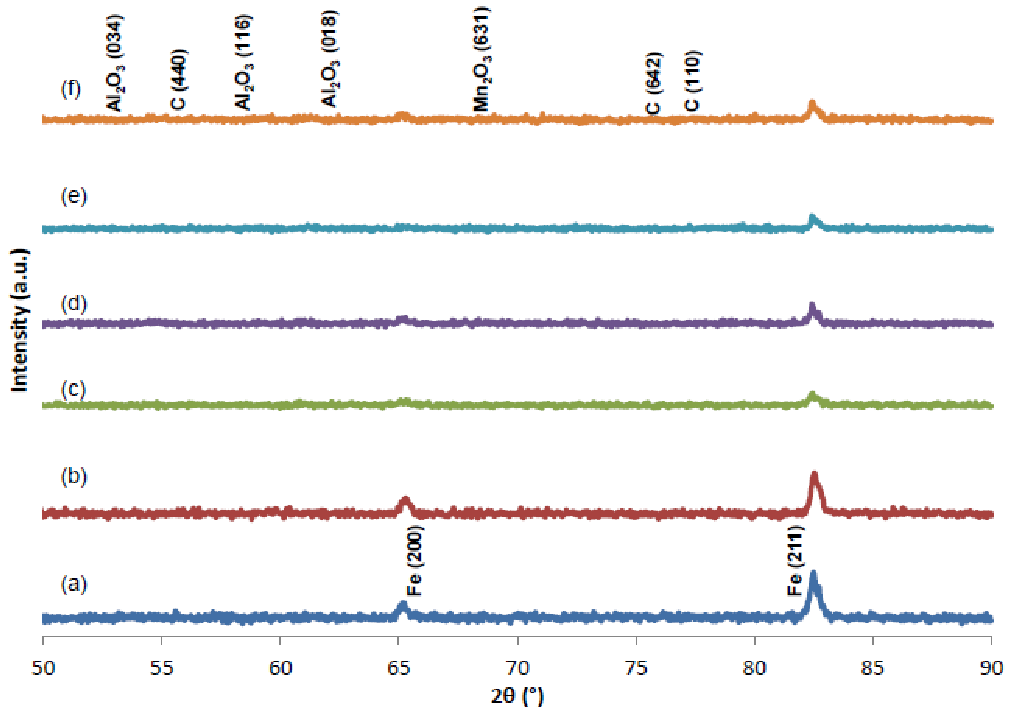

Figure 7. XRD peaks of (a) bare mild steel, (b) plain epoxy, (c) 10, (d) 20, (e) 25, and (f) 30 wt% CWM–epoxy resin conductive coating before exposure to 3.5 wt% NaCl solution in the OCP analysis.

Figure 8 shows the XRD peaks of bare mild steel and samples coated with CWM-epoxy resin system after being exposed to 3.5 wt% NaCl solution in the OCP analysis. Significant changes in the phase are observed for the bare mild steel after the immersion when the new peaks of iron hydroxide [$Fe(OH)_2$, ICDD 00-013-0089], iron chloride ($FeCl_2$, ICDD 01-070-1634), magnetite (Fe_3O_4, ICDD 01-079-0416), and haematite (Fe_2O_3, ICDD 01-089-7047) are recorded, which correspond to the corrosion products (Fig. 8a). In contrast, no additional phase appeared on the mild steel sample coated with plain epoxy and with 10 wt% CWM after exposed to 3.5 wt% NaCl solution, which proved that no corrosion products were detected (Figs. 8b and 8c). Besides that, the peaks of Fe still appeared on the XRD spectra and proved that Fe did not completely deteriorate or decompose into the other phase.

Similar changes occurred for the mild steel sample coated with 20–30 wt% CWM (Figs. 8d–8f). The original peaks of Fe diminished due to the oxidation of Fe into Fe^{2+} ions. The presence of Fe_2O_3 and Fe_3O_4 phases in the XRD analysis confirmed the formation of an oxide layer during the corrosion process. This result is in accordance with the morphological analysis as shown in Figs. 6d–6f, which determines the occurrence of iron oxide on these sample surfaces after they were immersed in 3.5 wt% NaCl. Among the four new phases, Fe_3O_4 is the major oxide, as evidenced by the fact that it had the most different peaks. Besides that, the presence of $FeCl_2$ phases at a few different peaks verified that the formation of metallic chloride also occurred during the polarization. Generally, these chloride ions are attracted by Fe^{2+} ions to preserve the electroneutrality [16].

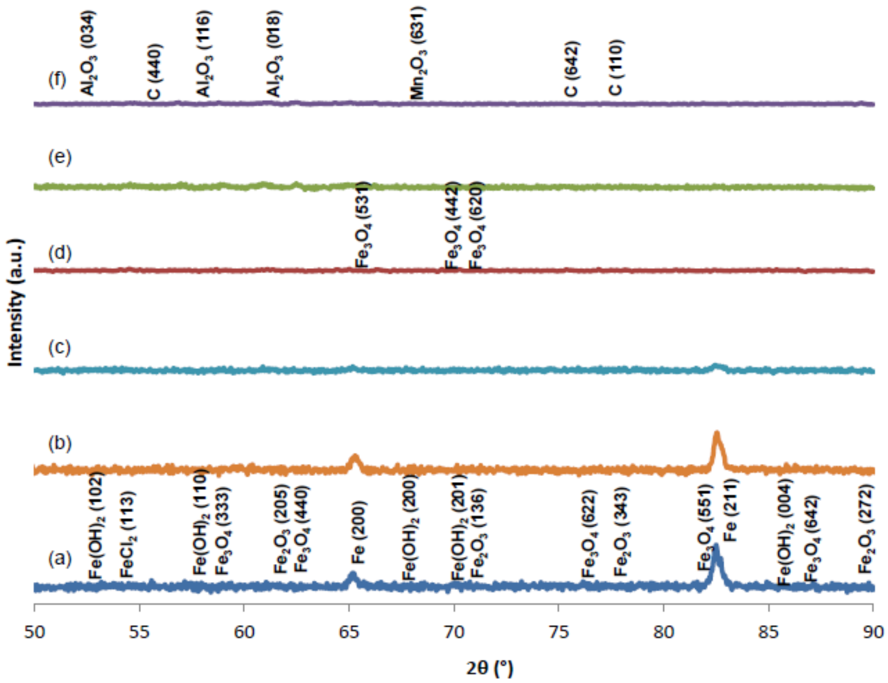

Figure 8. XRD peaks of (a) bare mild steel, (b) plain epoxy, (c) 10, (d) 20, (e) 25, and (f) 30 wt% conductive coating after exposure to 3.5 wt% NaCl solution in the OCP analysis.

The morphology and XRD analyses proved that the corrosion of mild steel occurred after 30 days of exposure to the corrosive environment. In the active corrosion region, Fe is dissolved in the anodic reaction while water and oxygen are reduced into hydroxide ions (OH^-) in the cathodic reaction. The electrochemical reactions involved are expressed as follows [16]:

Dissolution of iron: $Fe \rightarrow Fe^{2+} + 2e$ (4)

Reduction of oxygen: $O_2 + 4e^- + 2H_2O \rightarrow 4OH^-$ (5)

Overall corrosion reaction: $2Fe + 2H_2O + O_2 \rightarrow 2Fe^{2+} + 4(OH^-)$ (6)

Precipitation: $Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$ (7)

A film of solid hydroxide or oxide can be precipitated from an aqueous solution with the presence of metal ions in the solution. Therefore, a layer of $Fe(OH)_2$ or iron oxide such as Fe_2O_3 and Fe_3O_4 is formed at the surface of mild steel after giving away a water molecule through the reaction [16]:

$2Fe^{2+} + 3H_2O \rightarrow Fe_2O_3 + 6H^+ + 2e^-$ (8)

$3Fe_2O_3 + 2H^+ + 2e^- \rightarrow 2Fe_3O_4 + H_2O$ (9)

As a result, it is clearly indicated that only the mild steel sample coated with plain epoxy and with 10 wt% CWM can provide significant corrosion protection after 30 days of immersion in 3.5 wt% NaCl solutions.

4. CONCLUSIONS

The electrochemical properties of the conductive paint coatings depend on the content of CWM and the homogeneity of the surface of the coating. The addition of CWM improved the electrical conductivity with the maximum conductivity of 5.33×10^{-4} S cm^{-1} being obtained at 25 wt% CWM. Morphology scans show that the increase in conductivity was due to the distribution of filler, which allows electrons to flow either by direct physical contact of the filler particles or by a tunnelling effect for a length of a few nanometres. However, a reduction of corrosion potential was obtained in the corrosion analyses using high percentages of filler. The addition of CWM also increased the porosity of the conductive paint. Thus, it is shown that the addition of CWM content had opposing effects on the CWM–epoxy resin coating system when the high conductivity value contributed to the lowering of the corrosion resistance of the coated mild steel.

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