

## Anticorrosion Epoxy Coating Enriched with Hybrid Nanozinc Dust and Halloysite Nanotubes

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**ABSTRACT:** In this study, the performance of an epoxy coating with hybrid nanozinc dust and halloysite nanotube (HNT) fillers on the corrosion protection of a carbon steel substrate was investigated. The epoxy resin was mixed with a constant amount of nanozinc dust (1%) and different contents of HNTs (0, 0.5, 1, and 1.5%) with a high speed mixer. Fourier transform infrared spectroscopy and thermogravimetric analysis were used to analyze the interactions between the components in the coating material and the thermal stability of the epoxy coating, respectively. Open-circuit potential, salt spray testing, and microscopy were also used to assess the corrosion resistance of the carbon steel substrate coated with these coating materials. The incorporation of nanozinc in the epoxy coating enhanced the corrosion protection of the carbon steel substrate compared with the pure coating. Furthermore, HNTs further enhanced the corrosion protection. The best protection was achieved when 1% nanozinc and 1% HNT were used. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 955–960, 2013

**KEYWORDS:** coatings; resins; thermosets; clay

Received 22 November 2012; accepted 17 February 2013; Published online 17 April 2013

**DOI:** 10.1002/app.39239

### INTRODUCTION

For centuries, professionals had been looking for a solution to reduce the corrosion of metals. Corrosion is the deterioration of metal that is caused by the reaction of the metal with the environment.<sup>1</sup> Paint and coatings are great solutions for preventing corrosion. One-third of the production of paint is used to protect and decorate the metal surface. Paints and coatings can be divided into two categories, the convertible type, where they need a chemical reaction such as oxidation or polymerization, and the nonconvertible type, which are formed by the evaporation of the solvents. The former category includes alkyds, epoxy, esters, polyesters, urethanes, silicon, and other resins.<sup>2</sup>

Generally, the resin that is often used for coatings is epoxy. This is due to its outstanding processability, excellent chemical resistance, strong adhesion, and affinity to heterogeneous materials. However, the major disadvantages of pure epoxy resins are their brittleness and low fracture toughness.<sup>3</sup> The mechanical and thermal properties of epoxy resin can be further enhanced by the addition of additives. A new world of additives has been explored with the prefix *nano*. Many researchers<sup>4–9</sup> have reported that the incorporation of nanofillers in the epoxy coating structure results in increases in the barrier properties, thermal stability, fire resistance, transparency, color purity, and

resistance to organic solvents and in a lower coefficient of linear expansion.

Halloysite nanotubes (HNTs) are a kind of nanoclay that have been investigated as a type of additive and are mostly used as a reinforcement agent. Researchers<sup>10,11</sup> have reported that the use of HNTs in epoxies improved the properties of the resulting nanocomposites, such as the coefficient of corrosion protection, coefficient of thermal expansion, and modulus. Because of the polar nature of HNTs, they may have better compatibility with polar epoxy resin and are expected to be good reinforcement for epoxy binder. Liu et al.<sup>10</sup> showed that in a hybrid of epoxy resin with HNTs with increasing HNT content, the storage modulus increased, and this subsequently exposed excellent barrier properties of HNTs, which could ameliorate the corrosion protection of the substrate.

On the other hand, zinc has been used widely as an anticorrosive coating since 1840. This is due to the properties of zinc itself, which lead to a high anticorrosion efficiency. The incorporation of zinc in epoxy resin (zinc-rich paint) is a well-established method for protecting metal by cathodic protection.<sup>12,13</sup> Kalendová<sup>11</sup> reported that the smaller size zinc, such as nanozinc exhibited a higher efficiency in anticorrosion compared to the large size zinc on the microscale.

**Table I.** Detailed Formulations of the Coatings

Formulation name	Formulation content
H1	Plain epoxy (control formulation)
H2	Epoxy/1% nanozinc/0.0% HNT
H3	Epoxy/1% nanozinc/0.5% HNT
H4	Epoxy/1% nanozinc/1.0% HNT
H5	Epoxy/1% nanozinc/1.5% HNT

In this study, the effects of hybridization between the nanoparticulate zinc dust and HNTs in epoxy resin were investigated. Hybridization usually aims to attain a synergistic effect on the properties of epoxy resin and to reduce the production cost of advance materials.

## EXPERIMENTAL

### Materials

The epoxy resin and polyamide (hardener), Epicoate 1006 system, used in this study was purchased from Wee Tee Tong Chemicals Pte., Ltd. (Singapore), with a specific gravity of 1.11 with a hardener of polyamide. Sodium chloride (NaCl), xylene, and butanol were purchased from Bayer Co., Ltd. (Malaysia). The nanozinc dust was purchased from Guangzhou, Jiechuang Trading Co., Ltd. (China), as a gray powder containing 99.9 wt % zinc with a particle size of less than 100 nm. Meanwhile, HNTs were purchased from Sigma Aldrich Chemistry (Malaysia). The size of the material was between 50 and 100 nm.

### Preparation of the Epoxy/Nanozinc/HNT Coating

Table I shows the recipes of the primer formulation of the epoxy/nanozinc/HNT coatings that were used in this study. The epoxy resin was mixed with a constant amount of nanozinc powder (1% w/w), different amounts of HNTs (0, 0.5, 1, and 1.5% w/w), and a mixture of aromatic and alcoholic solvents (5% w/w) with a high-speed mixer at a speed of up to 2000 rpm to achieve a better distribution and dispersion of the nano-fillers. Lastly, the hardener (polyamide) was mixed with a homogeneous mixture with a ratio of 10:6 between the epoxy and the hardener. The mixture was then ready to be coated on the carbon steel substrate.

### Preparation of Carbon-Steel-Coated Substrate

The primers were applied on  $150 \times 100 \times 3$  mm<sup>3</sup> panels with a hole 6.5 mm in diameter applied at the center 10 mm from the top edge of the plate. These panels were duly abraded with emery paper and subsequently washed with tap water and rinsed with acetone to remove the remaining rust and impurities from the surface and dried. The prepared carbon steel substrate was coated by a brush and kept in a dry place at room temperature for 1 day to allow full curing; this led to the formation of a uniform coating on the substrate surface. All of the coated substrate was kept in desiccators to ensure that the substrate was free from any corrosion before testing.

### Testing

The sacrificial cathodic protection of coatings to protect the substrate was investigated by open-circuit potential (OCP) and salt spray testing. For OCP, the primed panels from one side

were completely immersed in a vertical position in a stationary aqueous electrolyte, including 3.5 wt % NaCl. The Ag/AgCl with 1M KCl used as a reference electrode and the potential calculated from voltmeter data. Only the surface of the plates was coated. The potential of the system and the surface of the steel was monitored regularly; the more positive  $E_{\text{corr}}$  value of  $-0.8$  mV/saturated calomel electrode (SCE)<sup>14,15</sup> and the generation of pitting on the surface signified the end of cathodic protection, respectively. Also, the coated plates with scratches (ASTM D 1654-79) were put in the automatic salt spray chamber for 240 h (ASTM B117), and we compared the corrosion of the plates in the scratched area at periods of 0, 120, and 240 h by optical microscopy and visual scanning.

The structural characterization of the final coating of materials was carried out by a PerkinElmer transmission Fourier transform infrared (FTIR) spectrometer with a resolution of  $4$  cm<sup>-1</sup>. The thermal stability of the coatings was evaluated by thermogravimetric analysis (TGA; PerkinElmer) at a heating rate of  $10^\circ\text{C}/\text{min}$  under a nitrogen atmosphere in a temperature range from ambient ( $22.5^\circ\text{C}$ ) to  $950^\circ\text{C}$ .

The conductance (electrical properties) of the coatings was evaluated by a multimeter with the probes in contact with the surface of the coating. The metal was protected galvanically by the zinc-rich epoxy coatings; moreover, the nanoparticulate zinc and HNT powders acted as good barriers to oxygen and water. A higher conductivity of the coating resulted in better corrosion protection. In consideration of the conductance evaluation, a multimeter with the probes in contact with the coating was used. The distance between the probes was 5 cm, and the standard deviation was found to be  $\pm 4.5\%$ . The corrosion rate was calculated by the measurement of the weight loss of the plates during the experimental period after the generated rusts were washed on the plates every day.

## RESULTS AND DISCUSSION

### Characterization of the Epoxy/Nanozinc/HNT Coatings

Figure 1 shows the FTIR spectra of the epoxy coatings. The spectra of FTIR that are shown in Figure 1 were recorded in the range of  $370$ – $4000$  cm<sup>-1</sup>. The functional groups of the coating could be determined by the point of absorption in the graph and were compared between all of the coating formulations. A broad peak in the range of  $3200$ – $3550$  cm<sup>-1</sup> was related to OH stretching from both the epoxy resin and HNT fillers. The stretching of C–H groups was achieved around  $3000$  cm<sup>-1</sup> for all of the coatings. The peaks illustrated between  $1500$  and  $1600$  cm<sup>-1</sup> corresponded to the C=C groups in the aromatic rings of the epoxy, and the peaks around  $1200$  cm<sup>-1</sup> were related to the deformation in units of C–O–C (aromatic) in epoxy. Finally, the peak around  $800$  cm<sup>-1</sup> corresponded to C–H of the aromatic groups, which belonged to all of the coating components.

It could be inferred from the graphs that the OH stretching ( $3200$  and  $3550$  cm<sup>-1</sup>) was attributed to the moisture attack in epoxy (H1 and H2). The addition of HNTs up to 1% (H3 and H4) led to increasing OH stretching because of the additional amount of OH groups from the HNTs. Du et al.<sup>16</sup> reported that HNTs consisted of a few hydroxyl groups (Si–OH) on the

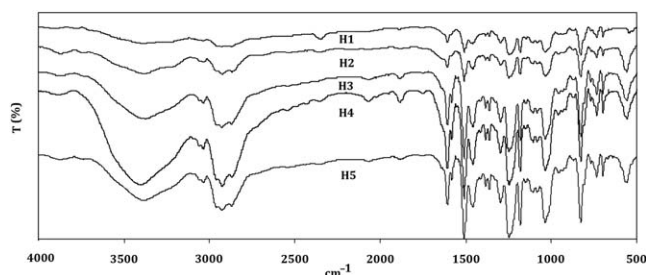


Figure 1. Comparison of the FTIR groups of the coatings.

surface and aluminol (Al—OH) groups in the inner tube (Figure 2). However, an increase in the HNTs up to a 1.5% content revealed a decrease in OH stretching. It is believed that at certain HNT content (H5), the OH group from its surface is enough to form hydrogen bonds with the epoxy resin, trap the epoxy, and thus reduce the OH groups in the coating materials; this is obvious in the FTIR graph of the coatings (Figure 1). However, a new peak appeared around  $600\text{ cm}^{-1}$  in the H2–H5 graphs, which could be attributed to ZnO.<sup>17</sup> This could have been caused by the generated layer, which imparted barrier properties from Zn.

#### Effect of the Nanozinc Dust/HNTs on the Thermal Stability of the Epoxy Coating

Figure 3 shows the TGA thermogram of the epoxy coatings. This graph indicates that epoxy coating with hybrid nanozinc dust/HNTs had a higher thermal stability compared to the epoxy coating only; this could have been due to the thermal stability of the metallic fillers and nanofillers. However, because of the low increment of filler contents, the differences were not very large. Table II shows the degradation temperature ( $T_{\text{deg}}$ ) at 80% weight loss and the percentage of char yield at  $500^\circ\text{C}$  for the epoxy coating. The epoxy coating with the highest amount of HNTs (1.5%) showed the highest  $T_{\text{deg}}$  compared to other epoxy coatings; this showed that this formulation had the highest thermal stability among the other samples. According to Pandey et al.,<sup>18</sup> the addition of small amounts of nanofillers proved to exert a thermal stabilization effect on a wide variety of epoxy matrices. Therefore, with the enhancement of  $T_{\text{deg}}$ , the thermal stability of the material also improved. With the percentage of char yield at  $500^\circ\text{C}$ , the highest thermal stability was for H5. The char yield was mainly attributed to the content of nanozinc dust and HNTs, which could stand temperatures above  $500^\circ\text{C}$ .

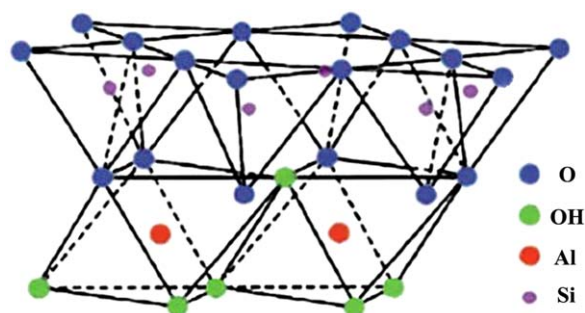


Figure 2. Schematically structure of HNT.<sup>16</sup> [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

This was due to the unique crystal structure of the HNTs, such as their rodlike geometry and the few alumina and silicates inside the structure,<sup>10</sup> and also the metallic element in the nanozinc dust. This clearly showed that at a higher loading of HNTs, the percentage char yield increased.

#### OCP Measurement (Corrosion Potential)

It is well-established that the duration of cathodic protection on the substrate can be measured via the corrosion potential. Thermodynamics have shown that the cathodic protection of steel is achieved when the potential is below than  $-0.8\text{ V/SCE}$ .<sup>14,15</sup> The measured potentials were the mixed potentials between the steel substrate and fillers, including the nanozinc and HNTs. In cathodic protection, the steel acted as a cathode, and the coatings, including fillers, acted as anode; by sacrificial (cathodic) protection, the coating corroded instead of the steel.<sup>13</sup> Depending on the activation of fillers in the coating, the anode area was bigger and affected the corrosion protection. The more active the pigment was, the higher anode area was, and this resulted in better protection.<sup>19</sup> The results show that up to a certain percentage, the fillers had synergism effect and the HNTs imparted interaction between the nanozinc fillers and helped with the cathodic protection.

The OCPs, which in an ideal case is identical to  $E_{\text{corr}}$  for the coatings, were plotted versus the immersion time in hours (Figure 4). We inferred from the graph that the duration of steel protection strongly depended on the nanozinc and HNTs. The results revealed that the epoxy coating (H1) after 96 h lost the stability for corrosion protection. The H2 resisted up to 120 h of testing; this might have been caused by the increasing conductivity of the coating on the substrate surface. An increment in the protection of the substrate was obvious with increasing HNT content from 0.5 to 1 wt % (H3–H4); this may have been due to the better interaction imparted between the zinc fillers, which also created a barrier layer to the metal surface. In comparison with H2, which had only nanozinc as a filler, H3 had a

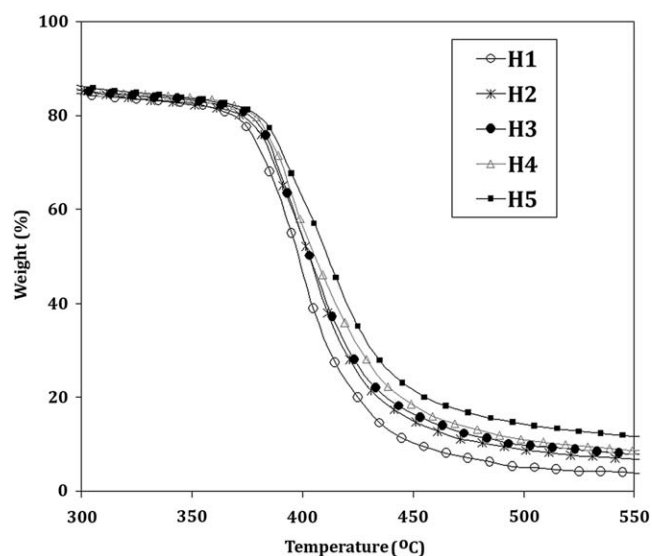


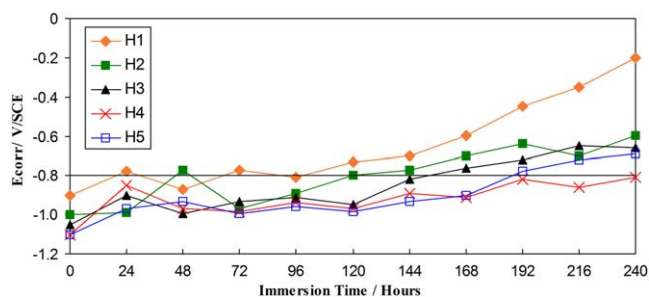
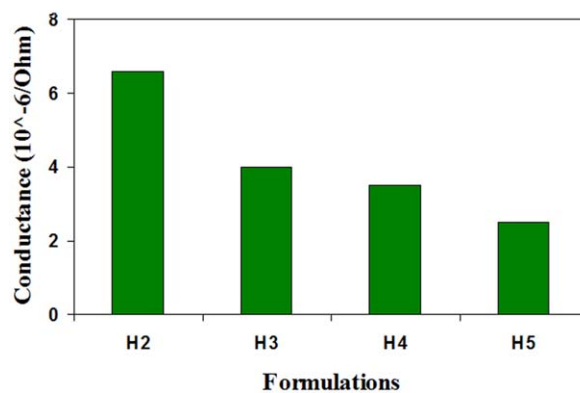
Figure 3. Thermal stability comparison curves for the hybridization nanozinc dust and HNT.

**Table II.** Comparison of the TGA Results:  $T_{80\%}$  and Char Yield Percentage Values

Composition	$T_{80\%}$ ( $^{\circ}\text{C}$ )	Char yield percentage (%) at $500^{\circ}\text{C}$
Epoxy	364.883	5.021
Epoxy/1% nanozinc	371.197	8.715
Epoxy/nanozinc/0.5% HNT	373.272	9.711
Epoxy/nanozinc/1.0% HNT	375.041	10.502
Epoxy/nanozinc/1.5% HNT	378.948	13.930

little better protection up to 144 h. This was evidence for the role of HNTs in improving the interaction between zinc fillers in epoxy. Moreover, with regard to another role of HNTs, Xie et al.<sup>20</sup> also showed that HNTs could reduce water percolation through the polymer film, and this could introduce barrier properties of HNTs to the coating. H4 and H5 showed resistance up to 240 and 192 h, respectively. It could be inferred from the graph that H4 (1 wt % nanozinc and 1 wt % HNT) showed the best protection between the others and, after which (H5), the properties decreased. This could have been caused by the synergism effect of the fillers imparted on the optimum filler content (H4) for the best protection by the cathodic and barrier properties of the nanozinc and HNTs, respectively. The reverse trend of protection in H5 made the hypothesis of filler agglomeration stronger by a greater loading of nanofillers; this was also obvious and was verified by FTIR results because of the OH groups on the HNT surface. The salt spray test and optical microscopy also showed the same trend in visual scanning and calculated area failed (Figure 6 and 7).

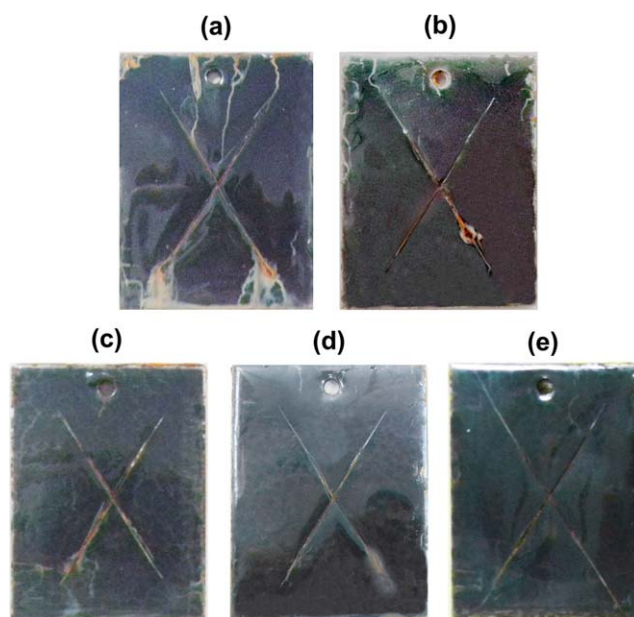
The conductance of primers with various concentrations of HNT and a constant amount of nanozinc powder is depicted in Figure 5. The addition of more nonconductive filler (HNTs) resulted in a reduction in the final coating conductance. It was obvious from Figure 5 that the conductance decreased drastically from H2 to H3, and this trend continued up to H5. This showed that the incorporation of HNT filler only introduced the barrier properties to primers and did not play a specific role in improving the cathodic protection; however, the hybrid effect of both fillers showed the synergism effect for better protection.

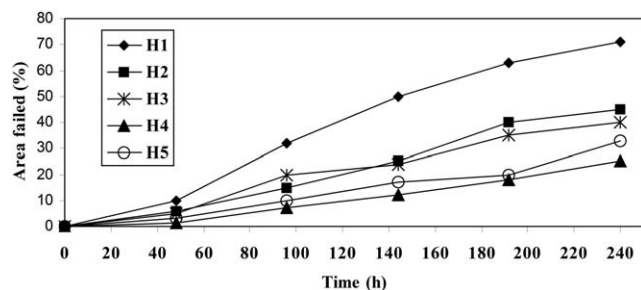
**Figure 4.** OCP of the coating plates versus immersion hours. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]**Figure 5.** Conductance versus coatings formulations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

### Salt Spray Test Results: Effect of Nanozinc Dust/HNTs on the Corrosion Resistance of the Epoxy Coating

Figures 6 show the different degrees of corrosion of the carbon steel plate after 240 h. The H1 plate showed a higher degree of corrosion compared to the other samples. As shown in Figure 6, with an increase in HNT loading, the plate had a reduced degree of corrosion. Epoxies with hybrid nanozinc dust and HNTs imparted a higher performance of corrosion protection compared with epoxy and nanozinc dust alone. This was due to the double action of the nanozinc as cathodic protection and HNTs, which provided good barrier properties to the epoxy coating materials.

Figure 7 illustrates the growth of the corroded area under the films versus time as calculated every 48 h according to the ASTM D 1654 with an optical microscope. It was inferred that the corrosion area in H1 hit the highest value after 240 h of exposure; however, in H4, the area failed was the best in

**Figure 6.** Plates after 240 h: (a) H1, (b) H2, (c) H3, (d) H4, and (e) H5. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

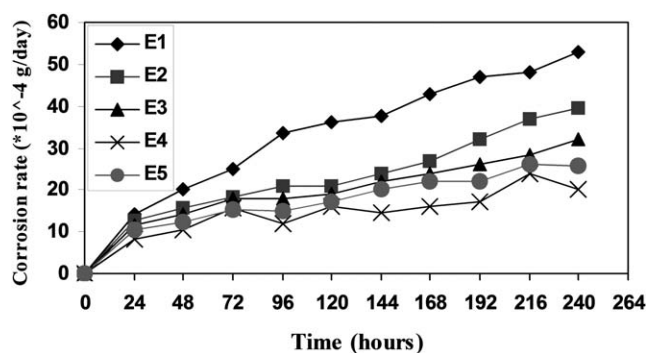


**Figure 7.** Comparison of the area failed versus time in the scratched plates according to ASTM D 1654.

comparison with the other formulations; this was fully consistent with the results obtained with the salt spray tests and FTIR spectroscopy. It was obvious that a reverse trend also happened in H5 in the area failed; this made the hypothesis of fillers agglomeration in 1.5 wt % HNTs stronger.

The data analysis of Figure 8 corroborated that H4 had the highest corrosion resistance. The increment of the HNT powder concentration in the hybrid with a fixed amount of nanozinc powder improved the protection and reduced the corrosion rate. Figure 8 compares the corrosion rate of coated plates. The corrosion rates were calculated via weight loss (in grams) per day. The corrosion rate showed the increasing trend of prevention up to 1 wt %, after which the reverse trend was observed. The data in the graph supported the salt spray, OCP, and area failed data for the trend of corrosion prevention.

As reported by Kalendová et al.,<sup>21</sup> the mechanism of zinc action was explained as cathodic protection on the basis of the electrochemical theory. The zinc coating acted as cathodic protection to protect the metal. On the other hand, some studies<sup>4,5,10,12</sup> have shown that the incorporation of HNTs in the epoxy coating structure results in an improvement in the barrier properties and the thermal stability as well as the resistance to organic solvents. The barrier layer, which was introduced by HNTs and generated ZnO, protected the substrate via the prevention of passing water and oxygen to reduce the corrosion of the metal surface. The greater observed corrosion in H5 in comparison with H4 was explained by the FTIR and OCP results; this was discussed earlier and could also be explained by the agglomeration of fillers in the primer. With regard to the fewer OH



**Figure 8.** Corrosion rate of the plates with coatings on weight loss (g) per day.

groups in this formulation, it may have caused a lower adhesion of the epoxy coating to the carbon steel substrate because of the fewer OH groups imparting hydrogen bonding on the metal surface. This phenomenon could have led to less corrosion protection of the coating materials and subsequently reduced the protection.

The HNT filler and generated ZnO sealed the pores in the coating and resulted in an amelioration of the barrier properties of the final coating.<sup>19</sup> In the case of H2, in which the only filler was 1% nanoparticulate zinc dust, the first vital role in corrosion prevention was played by the cathodic protection, and then, the generated barrier of ZnO improved the corrosion protection. However, in the other coatings, the cathodic and barrier protection acted simultaneously right from the beginning. Obviously, the best corrosion protection was obtained from the primers with 1 wt % HNTs. It was obvious that with H4, better protection was observed; this further enhanced the cathodic and barrier protection because of the improved connectivity within pigments and smaller void volumes. Hence, a very well synchronized cathodic and barrier protection was observed right from the beginning; this may have been responsible for the decrease in the corrosion rate of Zn and provided effective corrosion resistance to the base substrate for a prolonged period.

## CONCLUSIONS

Nanozinc dust and HNTs were found to be effective additives for lowering the corrosion rate and good for protecting a carbon steel substrate from corrosion. Nanozinc dust acts as cathodic protection in an ionic reaction. The addition of HNTs in the epoxy coating gave more advantages to prevent corrosion. In addition the lower prices of HNTs compared to other nanofillers, HNTs make a good barrier protector because of their unique structure, which can fill gaps and pores on the metal surface and make the HNTs more favorable. Different ratios of HNTs showed different potentials for corrosion protection and enhanced the thermal stability of epoxy coating material. The coating with H4 (1 wt % HNTs) gave a lower corrosion rate compared to all of the other formulations. The performance of the epoxy coating with hybrid nanozinc dust and HNTs was good for protecting the metal.

## ACKNOWLEDGMENTS

This research received no specific grant from any funding agency in the public, commercial, or not-for-profit sectors. However, the authors thank the Polymer Engineering Department of Universiti Teknologi Malaysia for their facilities and for giving them the opportunity to do this research.

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