Research Article

A New Approach in Modifying Polymeric Coatings to Increase Corrosion Resistance Properties

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Received 8 February 2013; Accepted 5 March 2013

Academic Editors: Y. Masuda, N. Uekawa, and R. A. Varin

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In this study, carbon steel sheets were coated with a modified epoxy coating. The urea-modified montmorillonite clay nanoparticles were added to a DGEBA epoxy resin in different contents and then applied to the surfaces. The corrosion resistance of the coated samples was determined by electrochemical techniques (open circuit potential and linear polarization) in 3.5 wt% NaCl solutions at room temperature and 80°C. Electrochemical impedance spectroscopy (EIS) evaluated the properties of polymer-coated metals and their changes during the exposure to corrosive environments. Scanning electron microscopy (SEM) was used to characterize the coatings. An improvement of protective properties of epoxy coatings with an optimal percentage of the modified clay in comparison with pure epoxy was achieved.

1. Introduction

Organic coatings represent one of the most effective methods to control metallic corrosion; however, less researches concerning the corrosion performance of coatings modified by clay nanoparticles have been reported so far, but during the last years, polymer-clay nanocomposites have attracted a lot of attention. Incorporation of a small amount (1–5 wt%) of clay into organic polymers leads to significant improvements in mechanical performance [1–5], thermal stability [6–11], barrier properties, and properties such as dimensional stability, reduced gas permeability, optical clarity, and flame retardancy of organic coatings [12–15]. According to the mentioned studies, these improvements are related to the morphology of the layered silicates. The most widely used layered silicate is montmorillonite (MMT). The crystallographic structure of MMT consists of two sheets of tetrahedral silica fused to an edge-shared octahedral-based sheet of either magnesium or aluminium hydroxide.

In order to improve dispersibility and protection properties of clay in the polymeric network, the surface of clay needs to be modified [11]. Using the inhibitors is one of the ways to modify the surface of clay (MMT). Even though there are

many nontoxic organic compounds which are effective corrosion inhibitors in solutions, for example, carboxylic acids or heterocyclic compounds, these inhibitors have not yet found wide usage in protective organic coatings. The reason for their lack of usage is that the active part of the compounds (e.g., $-\text{COOH}$) which is responsible for the formation of strong bonds with the metal surface, can also react with the polymer resins used to produce the coating [16]. Thus, the inhibitor is trapped by the polymer chain and cannot diffuse through the organic coating to reach the metal/film interface to prevent the corrosion reactions. Moreover, most of these organic inhibitors are soluble in water. This could cause blistering of the coatings when they are in contact with moisture. A solution to this problem is to bind the inhibitor molecules to the clay backbone and then disperse the modified clay in the organic coating. The inhibitors can then be slowly released at the metal/coating interface and react with the substrate to provide inhibitive protection [16].

Most of the investigations carried out on epoxy resin-(MMT clay) nanocomposites during the recent years have focused on the mechanical properties and thermal stability of these nanocomposites [17–22], and only few have examined the protective properties of epoxy resin-(MMT

clay) nanocomposites. In these studies, siloxane, quaternary ammonium, aminotrimethylphosphonic acid, and indole-3 butyric acid have been used as modifiers for nanoclay [13, 16]. In the present research, MMT clay was modified by urea and incorporated into an epoxy matrix. The protective properties of such epoxy coatings on carbon steel were evaluated using open circuit potential, linear polarization, and electrochemical impedance spectroscopy (EIS). Scanning electron microscopy (SEM) was used to characterize the coating structure and the presence of clay both at the steel/epoxy coating interface and the coating.

2. Experimental Procedure

2.1. Materials. The MMT nanoclay used in this study was obtained from Fluka Products. The diglycidyl ether of bisphenol A (DGEBA) epoxy resin (Araldite Razeen LR-2257) and a polyamide hardener (Aradure 43SBD) were purchased from Huntsman Corporation. Urea was purchased from Razi Chemical Products. Samples of carbon steel sheets ($10 \times 10 \times 0.8$ mm) were used as the substrate.

2.2. Preparation of Modified Clay and Coated Samples. A mechanical stirrer was used to disperse 7.0 g of MMT clay in 200 mL of distilled water. Afterward, 49.0 g urea was added, and the suspension was stirred in a thermostated water bath at 30°C for 24 hrs to obtain a white precipitate which was then filtered by filter paper. The urea-modified MMT clay was then dried at 23°C for 2 days. Then, to obtain a particle size of less than 100 nm, the filtered precipitate was ground first in a ball mill and then in a planet mill (high energy mill). The modified and ground MMT nanoclay was stored in a desiccator prior to application in the epoxy coating.

Abrasive papers with different grades from 80 to 800 were used to polish carbon steel sheets. Samples then were washed by water and cleaned with ethanol in order to be prepared for immediate application of the coating after polishing. In the next step, epoxy resin and epoxy hardener were mixed together to a defined ratio in accordance with the standard that the paint company has recommended for better efficiency in curing of the paint. For the current study, the utilized ratio for the components of the paint was from 4 to 1. Then, in various containers and with different percents of urea-modified clay, the coating was prepared for each sample. After mixing the components, there is just a one or 2 hrs time to apply the coating, otherwise it will be cured and would be useless. So it is better to prepare coatings which have various clay contents one by one. The urea-modified MMT clay was incorporated in the epoxy coating at five concentrations: 1 wt%, 2 wt%, 3 wt%, 4 wt%, and 5 wt% and stirred for 30 min. The liquid paints were applied by paint brush in a way that equal thicknesses were obtained for all samples. By changing the type of liquid paints according to its clay content, the paint brush should be changed to avoid the entrance of modified clay from each container to the next one. Samples were dried at room temperature for 48 hrs. These panels were ready for OCP, LP, and EIS tests and SEM.

TABLE 1: Open circuit potential values.

Sample	Clay (wt%)	OCP (V) 3.5 wt% NaCl solution	OCP (V) 3.5 wt% NaCl solution (80°C)
Bare	—	−0.55	−0.59
Pure epoxy	0	−0.54	−0.56
1	1	−0.46	−0.59
2	2	−0.45	−0.52
3	3	−0.40	−0.56
4	4	−0.52	−0.56
5	5	−0.52	−0.55

3. Results

3.1. Open Circuit Potential (OCP) Measurement. For each sample, open circuit potential (OCP) was performed for 30 min. To obtain this value, the sample was put in a 3-electrode cell being sure of connections establishment in the potentiostat set. GPES software was used to conduct the test. The OCP value is a criterion used to compare dissolution of samples in similar conditions within a solution.

3.1.1. 3.5 wt% NaCl Solution at Room Temperature and under Static Conditions. In the samples, as the modified MMT, clay level increased approximately up to 3% and caused the open circuit potential values to decrease which showed that the dissolution of samples is decreased. As modified clay content increased more than 3 wt%, the samples open circuit potential values gradually increased. According to Table 1, the open circuit potential values in the samples exposed to 3.5 wt% NaCl solution at room temperature and static conditions had numerically less potential than the ones in 3.5 wt% NaCl solution under high temperature. In another word, the samples in 3.5 wt% NaCl solution at room temperature were nobler, and the tendency to dissolution was lower.

3.1.2. 3.5 wt% NaCl Solution at High Temperature and under Static Conditions. The interesting point on the tests conducted at high temperature was that the samples showed approximately open circuit potential values close to each other. Results relevant to each of the samples in standard solution at high temperature have been shown in Table 1. The open circuit potential of the sample with pure epoxy coating and that of the samples with 3 wt% and 4 wt% modified clay showed equal values, that is, −0.56. It can be concluded from this process that at high temperatures, coatings behaviors with different modified clay percentages were approximately the same. These values have been much higher compared to the corresponding values for the samples under standard condition. These values were, in fact, indicative of more active open circuit potential values of the samples at high temperature. As a result, temperature showed its destructive effect on the samples.

3.2. Corrosion Rate and Linear Polarization Measurement

3.2.1. Samples in 3.5 wt% NaCl Solution at Room Temperature and under Static Conditions. For the samples in 3.5 wt% NaCl

TABLE 2: Corrosion rate values.

Sample	Clay (wt%)	CR (mm/yr) 3.5 wt% NaCl solution	CR (mm/yr) 3.5 wt% NaCl solution (80°C)
Bare	—	$4.852E-02$	$1.280E-01$
Pure epoxy	0	$1.053E-03$	$1.390E-02$
1	1	$7.348E-04$	$1.240E-03$
2	2	$6.898E-04$	$1.930E-03$
3	3	$2.349E-04$	$1.524E-02$
4	4	$2.804E-04$	$1.203E-02$
5	5	$2.904E-04$	$5.330E-02$

FIGURE 1: Linear polarization curves in 3.5 wt% NaCl solution.

solution under room temperature and static conditions, there was a regular trend in the corrosion rate decrease from the bare sample to the coated samples to the one contained 3 wt% modified clay. After this value, as the modified clay value increased, corrosion rate also gradually increased. According to Table 2, Figure 1, and OCP of these samples in 3.5 wt% NaCl solution and in 3.5 wt% NaCl solution at higher temperature, it was also clearly seen in the linear polarization diagrams that corrosion rates of the samples in 3.5 wt% NaCl solution at high temperature were totally more than of the ones at room temperature. It can show a dramatic decrease in protection properties of epoxy coatings containing modified clay at temperatures higher than the ambient conditions.

3.2.2. Samples Tested in 3.5 wt% NaCl Solution at High Temperature and under Static Conditions. As mentioned previously, in this series of samples, the samples' open circuit potentials showed nearly the same values. As it is observed in Table 2 and Figure 2, corrosion rate was reported to be higher for the samples tested in 3.5 wt% NaCl solution under high temperature and static conditions than the other group. Therefore, it can be observed that high temperature has influenced corrosion rate remarkably.

FIGURE 2: Linear polarization curves in 3.5 wt% NaCl solution at 80°C.

Generally, the prepared coating is partially heterogeneous and has a lot of micropores, which make the electrolyte penetration easier, but the addition of MMT nanoparticles may block the defects formed in previous operation, resulting in the formation of compact products and improvement of coating homogeneity. In addition, the clay may have condensation reaction with epoxy resin to form new cross-linking into the cured polymer network, resulting in the enhancement of coating compactness, and more important, better dispersion of nanoparticles in the epoxy resin. As seen in both environments, there is an optimal value for clay content in order to increase protective properties of the coating. The optimal content in ambient temperature is 3 wt% and at higher temperature environment is 1-2 wt%. After these optimal values which are critical pigment volume concentrations (PVCs), increasing the number of pores in the coatings may be a reason for decreasing the barrier properties of the coating [23].

3.3. Electrochemical Impedance Spectroscopy (EIS) Measurements. Over the past two decades, electrochemical impedance spectroscopy (EIS) has emerged as the most powerful electrochemical technique for investigating corrosion processes and for defining reaction mechanisms. One of the most successful applications of electrochemical impedance spectroscopy (EIS) has been in the evaluation of the properties of polymer-coated metals and their changes during exposure to corrosive environments [24]. It should be noted that the impedance is a quite complex resistance when a current passes through a circuit including resistors and capacitors [13]. One method to display the impedance values is the Nyquist method. The arc size in the Nyquist impedance chart represents the amount of charge transfer resistance. In fact, to obtain this amount, the intersection of the high-frequency end from the low-frequency end of the arc with the real axis must be subtracted. Based on the mechanism that the metal is protected, the diagram obtained in the Nyquist diagram will appear in different forms. The graph related

TABLE 3: Electrical impedance spectroscopy results.

Sample	Clay (wt%)	Imp (Ω) 3.5 wt% NaCl solution	Imp (Ω) 3.5 wt% NaCl solution (80°C)
Bare	—	2 k Ω	2 k Ω
Pure epoxy	0	500 k Ω	55 k Ω
1	1	1 M Ω	500 k Ω
2	2	11 M Ω	300 k Ω
3	3	90 M Ω	19 k Ω
4	4	3 M Ω	18 k Ω
5	5	1 M Ω	13 k Ω

to a metal with no coating has a loop in other words, it has one time constant. However, other coated metal samples have usually two loops or time constants in which the first is related to the organic coating used at high frequencies and the second one is related to reactions occurring on the metal at low frequencies. Parameters such as corrosion, use of organic coatings, penetration through the coating, and the surface roughness lead to the second time constant in the Nyquist diagram that can estimate the mechanism occurring in the coating [25]. Another way of showing data obtained from impedance test is using Bode diagrams that have been plotted and will be compared for all samples in both environments.

After putting the sample in a 3-electrode cell and ensuring connections establishment in the potentiostat set, the tests were conducted by using FRA software.

3.3.1. Samples in 3.5 wt% NaCl Solution at Room Temperature and under Static Conditions. Arc size in the impedance diagram indicate the amount of coating charge transfer resistance. Table 3 is related to the charge transfer resistance values of the samples in 3.5 wt% NaCl solution at the room temperature. As seen in Table 3, in 3.5 wt% NaCl solution at which the medium is standard, the coating charge transfer resistance is increasing from the bare sample toward the coated samples up to the coating containing 3 wt% modified clay. Additionally, as the modified clay values increased, after 3 wt%, the coating resistance decreased. These results showed obviously that, by using the modified clay, good protective properties can be acquired. These excellent anticorrosion properties can be due to the spread of clay-silicate nanolayers in epoxy and reducing the rate of water and oxygen penetration [11].

The interesting point is that this trend repeated nearly in this form for the OCP tests and the linear polarization tests which have been previously conducted. By studying the results obtained from the experiments in 3.5 wt% NaCl solution at room temperature and static conditions, it seemed that coatings resistance had generally higher values compared to the results obtained from the experiments in 3.5 wt% NaCl solution under higher temperature in static conditions.

3.3.2. Samples in 3.5 wt% NaCl Solution at High Temperature and under Static Conditions. As previously mentioned, in this group of samples, OCP test showed very close values to each other. Linear polarization tests gave similar results. For the

FIGURE 3: Bode curves in 3.5 wt% NaCl solution.

FIGURE 4: Bode curves in 3.5 wt% NaCl solution at 80°C.

samples in 3.5 wt% NaCl solution under high temperature, it is again observed as in Table 3, that coating charge transfer resistance was less than the previous samples, that is, the ones in 3.5 wt% NaCl solution at room temperature and static conditions. This conclusion was again in perfect compliance with the results of linear polarization and open circuit potential tests. The samples at high temperature had, thus, by no means the optimal characteristics of the ones at room temperatures. Yet, they had an irregular behavior, and as evidence showed, at high temperatures, epoxy coating with clay content ≤ 1 wt% behaved better than epoxy coating with higher percentages of modified clay, because as modified clay surpassed 1 wt%, coating resistance gradually decreased.

As previously noted, one other method to display impedance values is Bode method. To ensure the results obtained from the Nyquist diagrams, Bode charts were drawn for samples in both environments. In this diagram, the vertical axis illustrates the impedance values in $k\Omega\cdot cm^2$, and the horizontal axis shows the frequency values in kHz. By drawing the curves related to all samples in a Bode diagram, a logical comparison of the impedance values

FIGURE 5: SEM images of cross-section of the epoxy coatings containing 0–5 wt% of urea-modified clay ($\times 9000$).

can be performed. According to previous researches, with each sample that has higher impedance values at different frequencies, it can be concluded that this specimen had a better protective properties [13].

In case that we have only one time constant, that is when the sample is not coated, there is a line with negative slope, and in case that a polymer coating is applied such as epoxy, typically curves have two time constants and subsequently have two lines with negative slope in the curve.

By investigating the results of the studies, it was found that samples containing 2–4 weight percent of modified clay have shown better performance in this environment. This is evident because their curves were located at higher impedance values. As it is shown in Figure 3, by increasing the modified clay weight percent after 3%, the protective performance of the coating gradually decreased.

According to this figure, normally by applying an epoxy coating, the impedance values have increased to higher values for applied frequencies, and the charge transfer resistance of the coating has increased. Then, by adding modified clay from 1–3 weight percents, the curves peaked and showed better protective properties. To ensure this claim, the lines related to each sample can be extrapolated on the vertical axis to obtain the coating resistance which is similar to the height of the curve on the vertical axis. By increasing the amount of modified clay to four and five weight percent, the protective properties of the coating will drop due to the fact that maybe the coating is not able to accept more modified clay.

By plotting the Bode diagrams for the samples tested at high temperature environment, similar results obtained and confirmed the results from Nyquist method. As it is seen in Figure 4, in 3.5 wt% NaCl solution at high temperatures, with

increasing the weight percent of modified clay up to 2 wt%, protective properties of coating improved because the curves obtained are at higher impedance values [13], and then the protective properties of coating gradually declined. Thus, it was observed that at high temperatures according to previous tests done and the Nyquist diagram, epoxy filled with low percentages of modified clay showed better performance, but it was not comparable with the quality of the coating at room temperature.

3.4. Scanning Electron Microscopy (SEM) Analysis. Figure 5 illustrates the images taken by SEM from a cross-section of samples covered by an epoxy coating applied on carbon steel sheet surfaces. The purpose of taking these images was to investigate the effect of adding different percentages of urea-modified clay on the coating. In these images, Figures 5(a)–5(f) are, respectively, related to the pure epoxy-coated sample, the sample with epoxy coating containing 1 wt%, 2 wt%, 3 wt%, 4 wt%, and 5 wt% modified clay. It is clear that within the samples that there is modified clay in the epoxy coating; the structure is completely different from the pure epoxy coating sample both in appearance and the lamellar shape [16]. It is notable that the epoxy coating containing 3% modified clay is different in terms of structure occurred in comparison with other structures. The only thing that distinguishes the image obtained from this sample from that of other samples is that the structure of the coating in this case had more layer form, and it is in full compliance with previous investigations that had analyzed the protective properties of epoxy coatings containing modified clay as a function of lamellar structure [11, 16]. Therefore, this amount of modified clay is an optimum and maybe a maximum reception capacity of epoxy coating for a filler-like clay because by increasing the clay content, protective properties are gradually declined. This can be a confirmation for the properties discussed previously in this case on other tests.

From all the open circuit potential, linear polarization, electrochemical impedance measurements, and cross-section analysis, it can be concluded that the urea-modified clay plays an important role in the protective properties of epoxy coatings specially at room temperature.

4. Conclusion

Totally, it can be concluded that the performance of the epoxy coating at high temperature was reduced considerably, and low percentages of the modified clay (1% and 2%) have relatively better performance than other contents of modified clay. However, the application of this coating containing modified clay is not recommended at high temperatures. Furthermore, the coating in standard conditions has much better performance compared to conditions with high temperature, and the use of an epoxy coating containing 3 wt% urea-modified MMT clay is recommended in this situation. Finally, the results obtained in the 3.5 wt% NaCl solution at room temperature and 3.5 wt% NaCl solution at 80°C indicated an improvement of protective properties of epoxy coatings with an optimal percentage of the modified clay in comparison with pure epoxy. As it was specified, the pattern

of modified clay effectiveness on the samples in standard medium and in medium with high temperature was different. The mentioned optimum percentage of modified clay in the samples in 3.5 wt% NaCl solution was 3 weight percent, and for 3.5 wt% NaCl solution at 80°C, it was 1-2 weight percent of modified clay. The experimental results revealed a good correlation among OCP, LP, EIS, and SEM findings.

Conflict of Interests

The authors guarantee that no conflict of interests is followed in this paper. The authors are free from any financial or personal relationships or financial affairs that may result in the conflict of interests issue.

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