Optimizing Corrosion Protection of Stainless Steel 304 by Epoxy-Graphene Composite using Factorial Experimental Design

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Abstract

Epoxy-Graphene (E/G) composites were synthesized and evaluated as a corrosion protection coating on Stainless Steel type 304 (SS304) using in situ polymerization approach. Coatings were synthesized at various process variables in order to optimize the corrosion protection efficiency of the prepared protective E/G coating. Cyclic voltammetry (CV) electrochemical measurements were conducted to evaluate the protection efficiency of the prepared coatings. In addition, dispersion of graphene in the polymeric matrix was observed using Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). The study revealed that load of graphene as well as mixing time significantly influenced the corrosion protection efficiency, where the protection efficiency increased simultaneously with load of graphene.

Keywords
Corrosion, Graphene, Cyclic Voltammetry, Coatings, Design of experiment.

1. Introduction

A growing problematic natural problem in the metallic industry is corrosion, where metals deteriorate due to electrochemical reactions between metals and the surroundings. A growing number of studies focused on various corrosion protection techniques such as the design of advanced coatings that may significantly slow down corrosion rates and extend the lifetime of metals in different environments. Various materials such as nanocomposites, hydrophobic and organic-inorganic hybrid coatings have already been reported as a potential solution to extend the lifespan of metals [1] in addition to different approaches such as corrosion inhibitors [2], and anodic or cathodic protections [3]. The various protection technologies are currently utilized in fields such as construction, pipeline, and automobile industries.

Stainless steel 304 (SS304) is widely utilized in various fields of industry. This is attributed to the valuable properties of SS304 such as formability, weldability as well as the substantial thermal and electrical conductivity. Furthermore, SS304 may withstand different atmospheric conditions and temperatures up to 1650°F [4]; however, SS304 may corrode intensely in a chloride rich environment [5]. The incorporation of fillers in polymeric composites might slow the process of corrosion. The protection mechanism depends on the ability of the fillers to prolong the diffusion path corrosive agents follow to reach the surfaces of the metals. Graphene is material that has been increasingly investigated in the manufacturing of polymers composites. The growing interest in graphene is attributed to the ability of Graphene in enhancing mechanical, thermal and dielectric properties of different polymers [6], in addition to the low density and a very high aspect ratio of graphene compare to different fillers such as clay [7]. Therefore, graphene based materials have found wide applications in different fields including gas barrier application and the preparation of corrosion protective coatings [8-10].

The incorporation of graphene in epoxy may enhance the corrosion protection property of the polymer resin. However, there is no study that focuses on the influences of the E/G coating preparation variables on the corrosion protection property of the coatings. In the present study, the influences of the coating preparation variables such as load of graphene, mixing time, curing temperature and the thickness of coating are examined at high (+1) and low (-1) levels using a full factorial experiment design in order to maximize the corrosion protection efficiency of the E/G protective

coatings. Here, the corrosion protection efficiency of a coating is evaluated using electrochemical cyclic voltammetry measurements in a 3.5% aqueous Sodium Chloride (NaCl) solution.

2. Experimental

2.1 Materials

Polished SS304 foil (McMASTER-CARR) was used as substrate. Graphene, prepared by thermal exfoliation/reduction of graphite oxide was utilized (ACS Material). Graphene has surface area of 400-1000 m2/g and electrical resistivity of $\leq$ 0.3 Ω.cm According to the supplier. Bisphenol A diglycidyl ether (BADGE) and Poly(propylene glycol) bis(2-aminopropyl ether) (Hardner, B230) were supplied by Sigma Aldrich. All chemicals were used as received.

2.2 Composites Synthesis and Design of Experiment

The process of E/G composites preparation is schematically presented in Figure 1, where high and low loads of graphene sheets were first dispersed in (2.58 g) of the hardner (B230). The graphene suspension was sonicated/mixed at high and low levels before (3.82 g) of the epoxy resin was added to the suspension. The final solution was mechanically mixed and homogenized for 20 min each before it was spin coated at 300 rpm for 1 min and 4 min to produce thick and thin E/G coatings, respectively, on a SS304 substrate. Finally, the graphene solution on SS304 was thermally cured at high and low levels to produce E/G composite coated SS304 substrate.
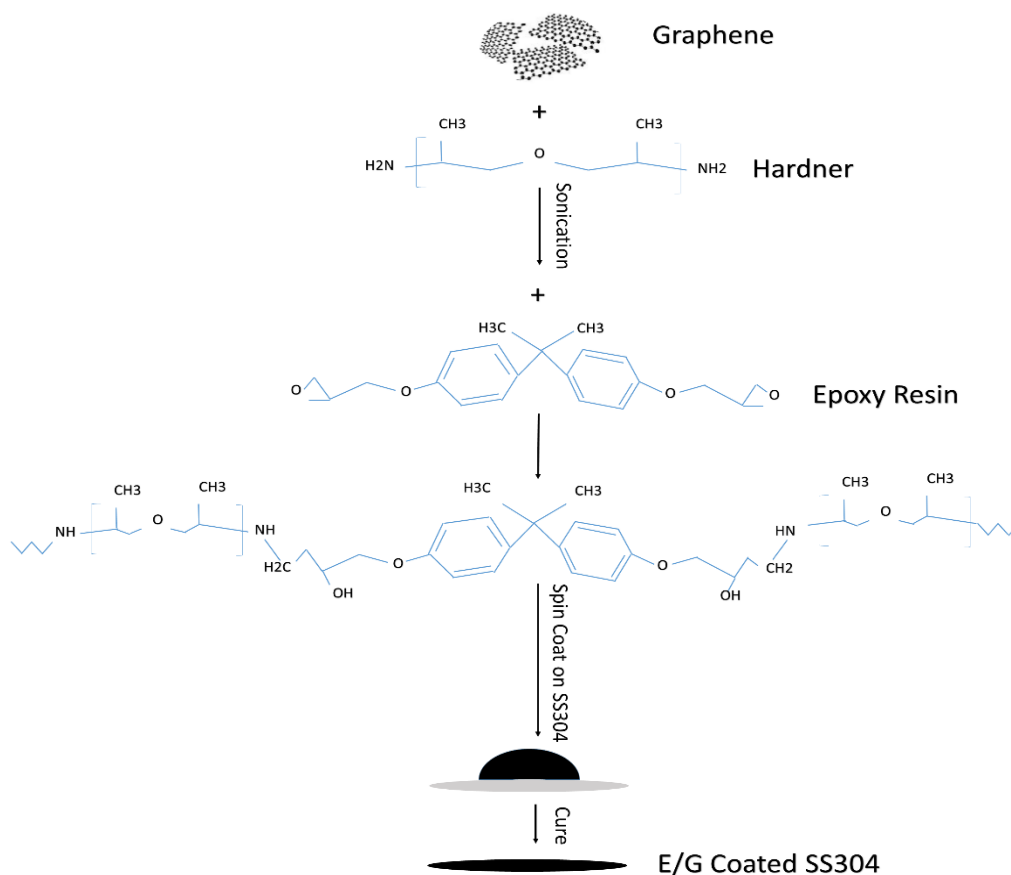

Figure 1. Synthesis and coating of E/G composites on SS304 substrates.

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E/G coatings were prepared at high (+1) and low (-1) levels of graphene loading, graphene /hardner mixing time, curing temperature and coating thickness as illustrated in Table 1.

Table 1. High and low levels of factors for factorial designed experiments

Factor	Name	High (+1)	Low(-1)
G	Load of Graphene (mg)	10	2
MT	Mixing time (min)	40	10
T	Curing Temperature ($^\circ$C)	70	40
TH	Coating Thickness (μm)	100	50

2.3 Electrochemical measurements

Electrochemical measurements were performed at 25 °C in a double-jacketed corrosion cell. One Liter 3.5% NaCl solution was used as electrolyte and experiments were conducted using a three electrode configuration, where the bare and coated SS304 substrates served as the working electrodes with 1 cm2 exposed surface area. Silver/Silver Chloride (Ag/AgCl) and two graphite rods were used as reference (RE) and counter electrodes (CE), respectively. The WE was first washed with acetone and distilled deionized water then, dried and installed in a Teflon sample holder. The open circuit potential was allowed to stabilize for 30 min after immersion of the WE in the electrolyte and after stabilization, the potential was recorded as the corrosion potential (Ecorr). Cyclic voltammetry (CV) technique was utilized to examine the electrochemical behavior of the bare and coated SS304 samples using a VSP-300 workstation (Uniscan instruments ltd.).

2.4 Morphology

Dispersion of graphene was observed using SEM (Zesis LEO 1550). In order to enhance the conductivity of E/G coating for SEM imaging, the coated SS304 substrates were further coated with gold using sputtering technique for 120 sec. The samples were fixed on SEM holders using carbon tape and the dispersion was captured at high and low magnifications. Graphene dispersion in the polymeric matrix was also observed using TEM (Philips CM-10 TEM), where E/G samples were collected by scrapping the coatings with a fine knife, dispersed in methanol for 5 min using sonication technique and collected with TEM copper grid. TEM collected samples were left to dry overnight under vacuum at room temperature.

3. Results

3.1 Cyclic Voltammetry

CV was used to record raw electrochemical data by scanning the potential of the WE from -0.5 to 0.5 V above the open circuit potential at 10 mV/min. This potential scanning generates Tafel plot, which permits the extraction of the corrosion current (I_{corr}) by extrapolating the straight portions of anodic and cathodic curves through E_{corr} as illustrated in Figure 2.
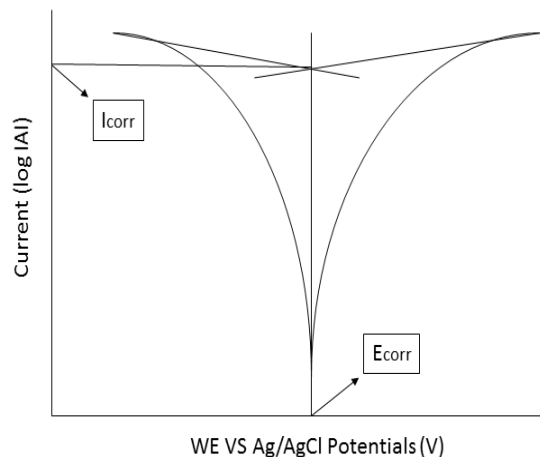
Figure 2. Synthesis and coating of E/G composites on SS304 substrates.

3.2 Influences of Synthesis Variables

2^4 full factorial design experiments were conducted in order to illustrate the significance of variable of the preparation process as well as the two factors interactions. The observed I_{corr} was reported for each experiment in Table 2 and in general, a drop in I_{corr} represent an enhancement in corrosion protection.

Table 2. 2^4 Design levels and corrosion currents

Run	Design Factors				$I_{corr}(\mu A/cm^2)$
	G	MT	T	TH	
I01	-1	-1	-1	-1	0.2
I02	+1	-1	-1	-1	0.007
I03	-1	+1	-1	-1	0.04
I04	+1	+1	-1	-1	0.0091
I05	-1	-1	+1	-1	0.19
I06	+1	-1	+1	-1	0.0086
I07	-1	+1	+1	-1	0.07
I08	+1	+1	+1	-1	0.0066
I09	-1	-1	-1	+1	0.3
I10	+1	-1	-1	+1	0.0098
I11	-1	+1	-1	+1	0.03
I12	+1	+1	-1	+1	0.0088
I13	-1	-1	+1	+1	0.25
I14	+1	-1	+1	+1	0.013
I15	-1	+1	+1	+1	0.05
I16	+1	+1	+1	+1	0.001

Analysis of variance (ANOVA) approach was adopted to analyze the factorial design experimental and the results are presented in Table 3. The total sum of variance was calculated using equation 1, where yi and n represent the response of experiment I and the number of experiments, respectively. Furthermore, the sum of square (SS) for each factor and their interaction was calculated using equation 2, where k is the number of main factors.

Table 3. Analysis of variance for main Effects and two-factor interactions for observed response

Factor	Effect	SS	df	MS	F
G	-0.133	0.07	1	0.07	14.2[*]
MT	-0.095	0.036	1	0.036	7.2[*]
T	-0.002	$1.5e^{-5}$	1	$1.5e^{-5}$	0.003

TH	0.016	0.001	1	0.001	0.2
G×MT	0.092	0.03	1	0.03	6.79*
G×T	0.001	$1.3e^{-6}$	1	$1.2e^{-6}$	$2.5e^{-4}$
G×TH	-0.016	0.001	1	0.001	0.2
MT×T	0.012	$0.5e^{-3}$	1	0.0005	0.11
MT×TH	-0.025	0.003	1	0.003	0.51
T×TH	-0.007	$0.2e^{-3}$	1	0.0002	0.03
Error	-	0.017	5	0.003	-
Total	-	0.164	15	-	-

*Significance factors.

$$SS_{total} = \sum_{i=1}^{n} y_i^2 - (\sum_{i=1}^{n} y_i)/n \qquad (1)$$

$$SS_{effect} = 2^{k-2}(effect)^2 \qquad (2)$$

The error sum of square was computed as the difference between the total sum of square and the summation of the sum of squares for main factors and their interactions. The degree of freedom (df) for factors and their interaction is the levels of factors less one. Therefore, main factors degree of freedom is (2-1), while, the interactions degree of freedom is (2-1) × (2-1). The error sum of square degree of freedom equal the total number of experiments less the sum of all main factors and interaction effects less one (16-10-1=5). Finally, the degree of freedom of the total sum of square is the number of experiments less one (16-1=15). The mean squares (MS) are compute by dividing the sum of square over the degree of freedom and the F values for a main factor or an interaction is calculated by diving the mean square of the main factor or the interaction over the mean square of the error. At 95% confidence interval ($F_{1,5}$=6.61) a main factor or an interaction is considered significant when the F value is grater then 6.61 and not otherwise.

From the reported analysis in Table 3, it can be observed that load of graphene, mixing time and the interaction between these factors are significant. The importance of the significant factors can be observed in the results reported in Table 2, where the corrosion current drop when the load of graphene is high indicating an enhancement in corrosion protection. The same observation was noted for mixing time, where the corrosion current always drops at high mixing time. Finally, it was interesting to observe that at low load of graphene, increasing the mixing time excelled protection by attenuating the corrosion current. The interaction effect between the load of graphene and mixing time is explained in Figure 3, where corrosion currents are always low at high load of graphene, while the corrosion currents were high and low when a low and high mixing times were used at a low load of graphene.

The enhancement in corrosion protection efficiency can be attributed to the ability of graphene in prolonging pathways corrosive elements follow to reach metal surface and increasing the mixing time may help enhancing the dispersion of graphene and consequently advance corrosion protection property of the E/G coating.
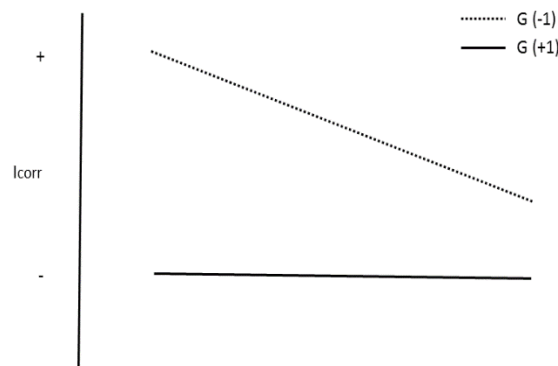

Figure 3. Interaction effects between load of graphene and mixing time.

3.3 Morphology

Dispersion of graphene in Epoxy resin was observed using SEM and TEM. Figure 4 (a and b), depicts the dispersion of graphene in samples I02 and I04, where the loads of graphene were high, while the mixing times were low and high, respectively. From the figures, it can be observed that in both cases graphene sheets were widely dispersed regardless of the mixing time. In contrast, graphene sheets were not always widely dispersed when a low load of graphene was incorporated in the polymeric matrix. This can be observed in Figure 5 (a and b), which depicts the dispersion of low loads of graphene in samples I03 and I01, where the mixing time is high and low, respectively. Here, graphene sheets were well dispersed in sample I03, where mixing time was high as presented in Figure 5a, while stacks of graphene sheets were observed at low mixing time in sample I01 as shown in Figure 5b. The observed degree of dispersion of graphene in evaluated samples support the significance of the load of graphene, the mixing time and the interaction between the two factors as reported in previous section. The widely dispersed graphene sheets extend the pathway corrosive agents follow to reach SS304 substrates and consequently enhance the corrosion protection properties of the coatings.
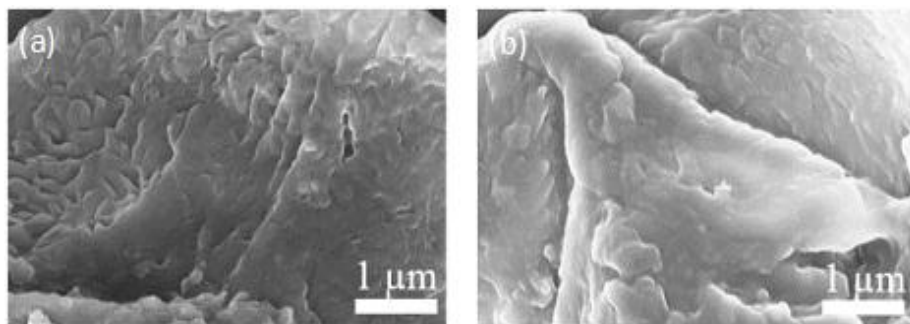

Figure 4. SEM images of graphene dispersion in (a) I02 and (b) I04 .
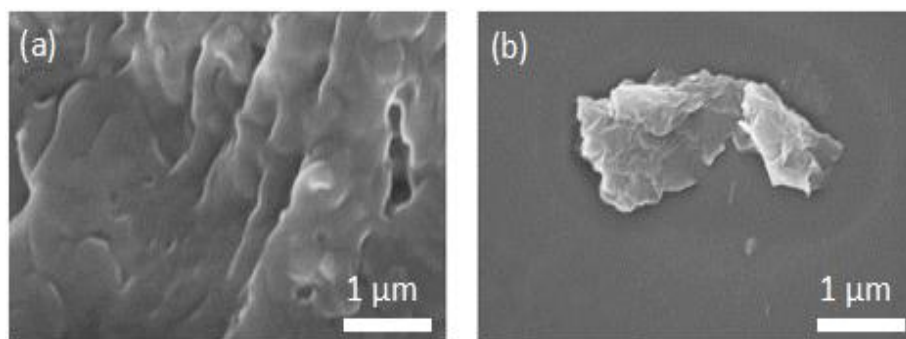

Figure 5. SEM images of graphene dispersion in (a) I03 and (b) I01 .

TEM was also utilized to observe the dispersion of low loadings of graphene at high and low mixing times in samples I03 and I01 as depicted in Figure 6 (a and b), respectively. The observed thin sheets of graphene in Figure 6a confirms that increasing mixing time resulted in a better dispersion of graphene sheets. In contrast, the low mixing in sample I01 resulted in poor exfoliation of graphene sheets, which can be observed as thick stacks of graphene sheets in Figure 6b.
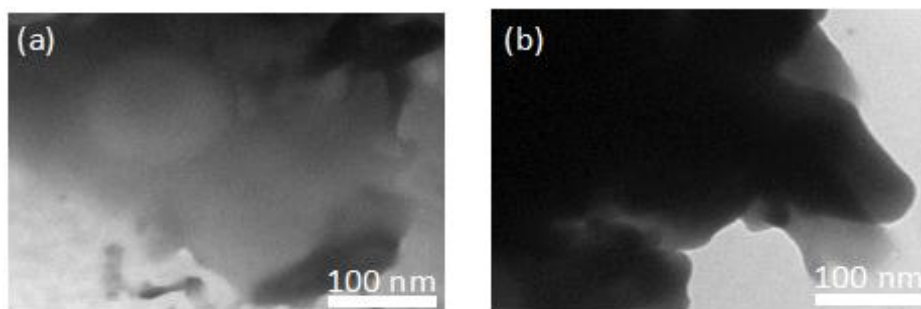
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Figure 6. TEM images of graphene dispersion in (a) I03 and (b) I01 .

4. Conclusion

A full factorial experimental design study was conducted to optimize corrosion protection property of Epoxy/graphene composites coatings on SS304 substrates. Influences of the preparation parameters, which include load of graphene, mixing time, curing temperature and coating's thickness on the corrosion protection properties of the coatings were evaluated at two levels using CV technique. E/G coatings were prepared by thermal curing, where in situ polymerization approach was utilized to incorporate graphene sheets in the epoxy matrix. The dispersion of graphene was captured using SEM and TEM techniques at high magnification. The study revealed that addition of graphene enhances the corrosion inhibition abilities of E/G coatings. Furthermore, it was concluded that load of graphene, mixing time and the interaction between those two parameters have significant influences on the corrosion protection properties of the E/G coatings. The enhancement in the protection properties was attributed to degree of dispersion of graphene in the matrices as presented in the SEM and TEM images, where graphene sheets may prolong the pathways corrosive agents cross to reach the metals and coatings interfaces.

Acknowledgements

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Biography

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