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CORROSION PROTECTION OF STAINLESS STEEL TYPE 304 USING GRAPHENE COMPOSITES

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Abstract

Polyetherimide-Graphene (PEI/G) composites were prepared using in situ polymerization approach and thermally cured under vacuum on Stainless Steel 304 (SS304) substrates in order to be evaluated as corrosion protection coatings. Several steps curing were performed to ensure complete imidization of PEI/G composites. Dispersion of the graphene fillers in the PEI matrices was captured using Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM). The study examines PEI/G composites as corrosion protection coatings using electrochemical techniques such as Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS). Furthermore, the influences of the load of graphene on the electrochemical behavior as well as the interface adhesion of the PEI/G composites are illustrated. Adhesion tests were conducted and evaluated according to ASTM D3359 standard and the long term performances of the prepared PEI/G coatings were confirmed by conducting the adhesion tests after 30 days of exposure to the corrosive medium. The study revealed that PEI may slow down the corrosion process on SS304 substrates and this protection property of PEI can be excelled by the incorporation of graphene in the PEI matrix.

Keywords

Graphene, Corrosion, Adhesion, Coating, Electrochemical

1. Introduction

Currently the world relies heavily on the metallic finishing industry to produce quality products that are both durable and long lasting. One of the prominent challenges in this industry is corrosion which is the process by which electrochemical reactions cause a material to deteriorate as it reacts with its environment. This detrimental process is costly and it is hugely affecting the economy of today's industrial nations. Researchers have been taking initiative to develop corrosion resistant coatings and materials that are affordable and practical. Nano-composites, hydrophobic and organic-inorganic hybrid coatings are all examples of anticorrosion developments that have shown success by increasing the lifespan of materials (Guo et al., 2012). Based on research by Moretti et al. (2004); Shen et al. (2005), corrosion inhibitors and anodic and cathodic protections are being developed and used to minimize corrosion. Despite the vast research occurring in the field of corrosion, there is still a need for a less costly and more effective way to deal with corrosion's consequences.

A material commonly used for the testing of anticorrosion coatings is stainless steel 304

(SS304). SS304 corrodes intensely in sodium chloride solution making it ideal for testing and research (The International Nickel Company Inc., 1963). SS304 also conducts heat, electricity, and it is formable and weldable. Additionally, it is a very durable material as evident by its ability to withstand temperatures as high as 1650 °F as well as a wide range of atmospheric conditions (Kang et al., 2005). It is shown that fillers in polymeric composites serve more purpose than just reducing corrosion. Studies done in the 1960s on polymer based composites describe how the composites might also strengthen the pre-existing mechanical properties of the material. This was especially true when nanofillers made with inorganic compounds formed organic-inorganic nanocomposites. These nanocomposites were in layered, tubular, and spherical forms such as clay, carbon nanotubes and silicon dioxide. The poor adhesion between polymeric substances and metal substrates makes corrosion protective coatings impractical (Roy et al., 2007). However, a solution was found via the use of polyetherimide (PEI). PEI is a solid candidate for use in anticorrosion coatings as it is a polymeric material with qualities such as high chemical and thermal stability, a low dielectric constant, a low thermal expansion coefficient, and the ability to withstand high temperatures (Crosby & Lee, 2007).

In efforts to improve the quality of polymer composites, graphene is being used more and more by researchers for their studies. Graphene not only provides greater mechanical, thermal and dielectric properties, but it also has a relatively low density and high aspect ratio in comparison to other nanofillers (Potts et al., 2012). Past and present studies are functionalizing graphene and forming it into various materials such as nanosheets and nanoplatelets (Xu & Buehler, 2010). Therefore, graphene has formed a wide range of applications in both anticorrosive coatings and gas barriers (Chang et al., 2012; Chang et al., 2014; Singh et al., 2013; Chang et al., 2012; Prasai et al., 2012). Although graphene and PEI evidently have valuable properties, limited research has been conducted demonstrating the use of both materials in tandem to form anticorrosive coatings for the protection of stainless steel 304.

The main objectives of this study are:

- Synthesis of graphene-PEI (PEI/G) composites and investigates its success as an anticorrosive coating on stainless steel 304.
- Confirm the long term performances of the prepared protective PEI/G coatings.

The PEI/G composite works to protect the stainless steel 304 from air and water, which are two major factors that contribute to corrosion. The graphene nanosheets within the PEI

matrix also serve to lengthen the diffusion pathway for corrosion-causing agents, therefore slowing down the corrosion process. The effectiveness of this coating is measured using electrochemical corrosion measurements in a 3.5% aqueous sodium chloride solution which serves to show the corrosion inhibition ability of the graphene-PEI nanocomposites.

2. Materials and Methods

Materials

Stainless steel 304 foil was obtained for this experiment from Mc-Master-Carr. A single layer graphene with surface area of 400-1000 m²/g and electrical resistivity of $\leq 0.3 \Omega \cdot \text{cm}$ was obtained from ACS Material. This single layer graphene was prepared by execution of the modified Hummer technique which involves thermal exfoliation/reduction of graphite oxide (Ojha et al., 2014). 4,4-Bisphenol A Dianhydride (BPADA) was supplied by Polysciences Inc. and was first put under vacuum at 60 °C for 3 hours in order to remove moisture. Finally, m-Phenylenediamine (mPDA) and N-Methyl-2-pyrrolidione (NMP) solvent were obtained from Sigma-Aldrich.

Composite Preparation, Coating, and Curing

The procedures for the preparation of polyetherimide-graphene composite coatings are outlined below and illustrated in (Figure 1).

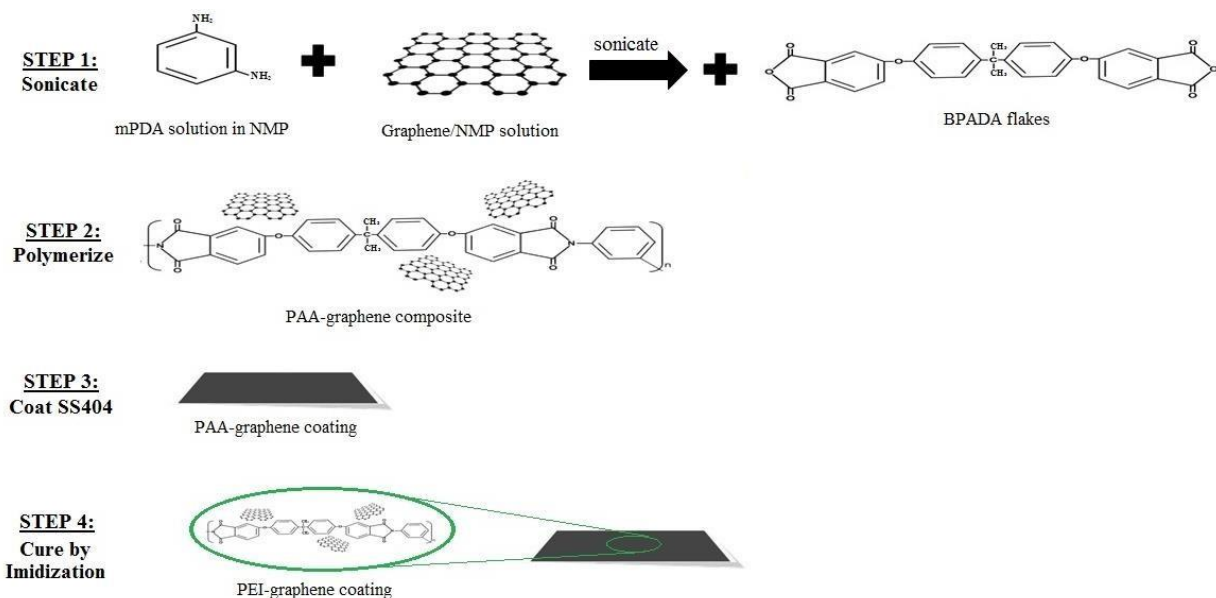


Figure 1: A schematic of the synthesis of PEI/G composites by in situ polymerization approach.

In preparing the composites with 0.1 wt. % graphene (PEI/G_{0.1}) coating, 6.4 mg of

graphene and 35 mL of NMP solvent were mixed for 1 hour using a magnetic stirrer and then bath sonicated for another hour. Next, 1.1 g of mPDA was mixed with 35 mL of NMP until the solution became clear. The prepared solutions were combined and stirred for one hour and sonicated for an additional hour. 5.3 g of BPADA was mixed into the resulting solution and left to react overnight to ensure that the reaction went to completion. Using a brush, the mixture was spread onto a clean SS304 plate and a film applicator (Paul N.Gardner Co. Inc.) was used to maintain a thickness of 50 ± 1 μm . The coated substrate was left under vacuum at 70 °C for 10 hours to evaporate the NMP solvent. Next, the coated substrate was heated at 100 °C, 150 °C, and 205 °C, respectively, each for two hours. Finally, the coated SS304 was placed in the vacuum to cool to room temperature. Same procedures were followed to prepare 0.5 wt. % graphene (PEI/G_{0.5}) and 1 wt. % graphene (PEI/G₁) coatings using graphene loadings of 32.2 mg and 64.6 mg, respectively.

Adhesion Test

The adhesion test was accomplished using a tape test kit (Paul N. Gardner Company Inc.) consisting of an 11-tooth blade with 1 mm spacing and it was carried out as directed by the ASTM-3359D standards (ASTM International, 2009).

Morphology Characterization

The dispersion of the graphene fillers in the hosting polymeric matrix of the graphene composite coating were examined using SEM (Zeiss LEO 1550). The substrate was held in place in the SEM holder using carbon tape and then gold coated by sputtering for two minutes. The dispersion of graphene on the PEI matrix and the morphology of the coating were analyzed by TEM (Philips CM-10 TEM). The PEI/G coating sample was acquired and prepared by first removing it from the SS304 substrate with a sharp blade, and then soaking it in methanol for 5 minutes, collecting it with a TEM copper grid, and drying it overnight in a vacuum at room temperature.

Electrochemical Measurements

VSP-300 workstation (Uniscan Instruments Ltd) containing a double-jacketed corrosion cell with a three-electrode configuration was used for electrochemical measurements. The corrosion cell was covered with a Teflon plate with drilled holes for placement of the electrodes. The configuration consisted of two graphite rods serving as counter electrodes (CE), a circular SS304 substrate as the working electrode (WE), and silver/silver chloride (Ag/AgCl) as the reference electrode (RE). Prior to use, the SS304 sample was cleaned and rinsed with acetone

and deionized water, respectively. The SS304 specimen was then secured in the Teflon sample holder with an exposed area of 1 cm^2 and left to stabilize at room temperature in the 3.5% NaCl electrolyte solution prior to testing. To ensure greatest accuracy, all measurements were repeated three times.

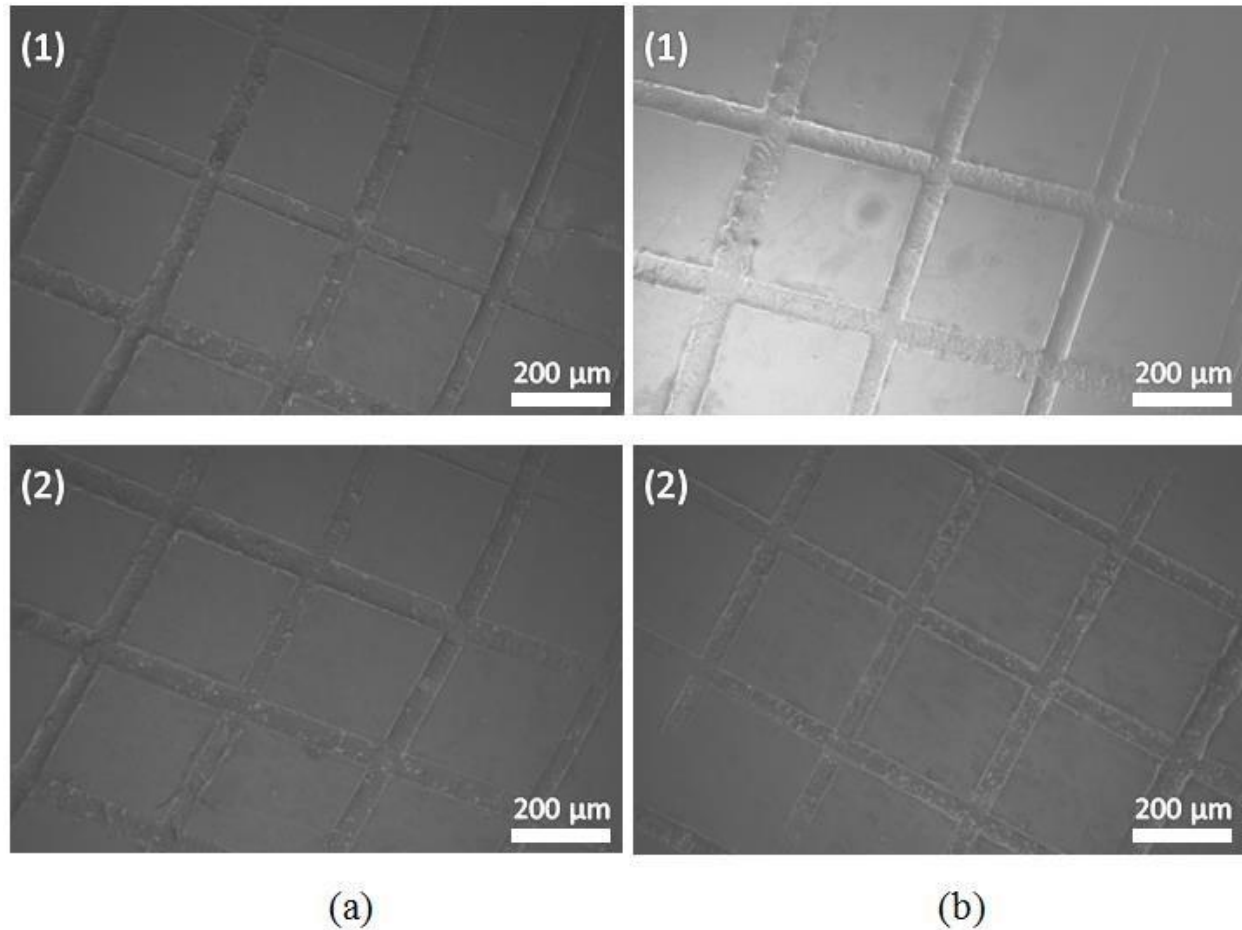


Figure 2: Post-adhesion tests images on (1) PEI/G_{0.1} and (2) PEI/G_{0.5} coatings (a) before and (b) after 30 days of exposure to the 3.5% NaCl solution.

Bio-Logic EC-Lab software was used to obtain corrosion potential (E_{corr}) and corrosion current density (I_{corr}). Data was presented via Tafel plots with scan range of 10 mV/min and at a range of -500 mV and +500 mV above the corrosion potential. The open circuit potential at equilibrium state was represented as the open circuit potential (in mV) against the reference electrode. I_{corr} was determined by extrapolating the linear parts of the Tafel plot to E_{corr} .

Bio-Logic EC-Lab software was also used to generate Nyquist plots for electrochemical impedance measurements. Data was plotted at a frequency range of 100 kHz to 100 MHz.

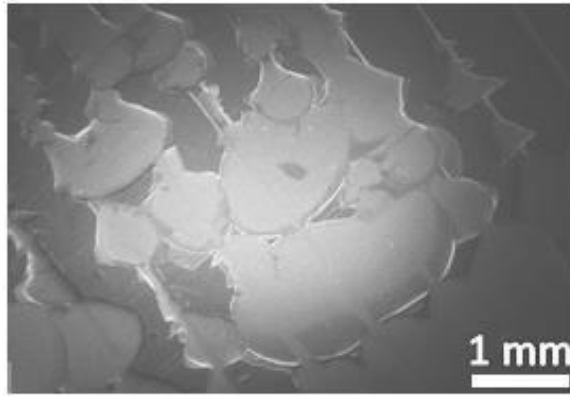


Figure 3: Post-adhesion test image on PEI/G₁.

Corrosion rate (R_{corr}) was calculated using equation (1) and according to ASTM standard G102 (ASTM International, 2010).

$$R_{corr} = \frac{0.13 \times I_{corr} \times EW}{A \times \rho} \quad (1)$$

Where: ρ is the density of SS304 (8.03 g/cm³), A is the sample area (1 cm²), and EW is the equivalent weight of SS304 (25.12 g).

3. Results

Adhesion

Corrosive agents may accumulate at the interface between a coating and the coated metal substrate. Therefore, it is essential to examine the interface adhesion before considering a coating for any purposes including corrosion protection. Here the adhesion test was carried out according to the ASTM D3359 standard with tape test kit. Furthermore, the long term performances of the PEI/G_{0.1} and PEI/G_{0.5} coatings were examined by performing the adhesion test after exposing the coatings to the 3.5% NaCl solution for 30 days. Figure 2, depicts the SEM post adhesion tests images for PEI/G_{0.1} and PEI/G_{0.5}, where no peeling were observed in all images and both coatings received a 5B rating according to the ASTM standard.

Moreover, it was interesting to observe the influences of increasing the loading of graphene on the interface adhesion property of the PEI/G composites. Here, the excess load of graphene resulted in loss of interface adhesion as presented in (Figure 3), where more than 65% of the PEI/G₁ coating was peeled off after conducting the adhesion test and the coating received a 0B rating according to the ASTM standard. No further studies were performed on PEI/G₁ composite due to the poor interface adhesion property of the composite.

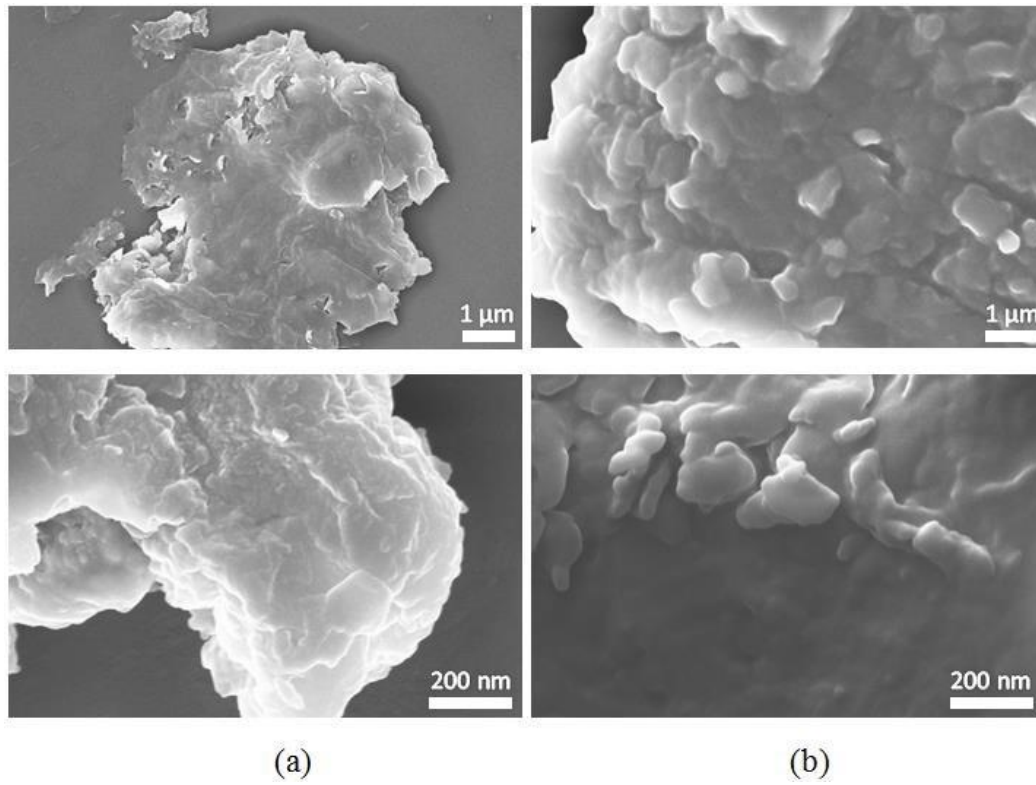


Figure 4: SEM Images for Dispersion of graphene in (a) PEI/G_{0.5} and (b) PEI/G_{0.1} composite.

Morphology

Dispersion of the graphene sheets in the polymeric matrices was studied using SEM and TEM at high and low resolution as depicted in Figure 4 and 5, respectively. The images demonstrate well dispersed graphene sheets in both PEI/G_{0.1} and PEI/G_{0.5}. However, thin graphene sheets were observed in PEI/G_{0.1} compare to thick stacks of graphene in PEI/G_{0.5} and this can be linked to the smaller loading of graphene in the former composite.

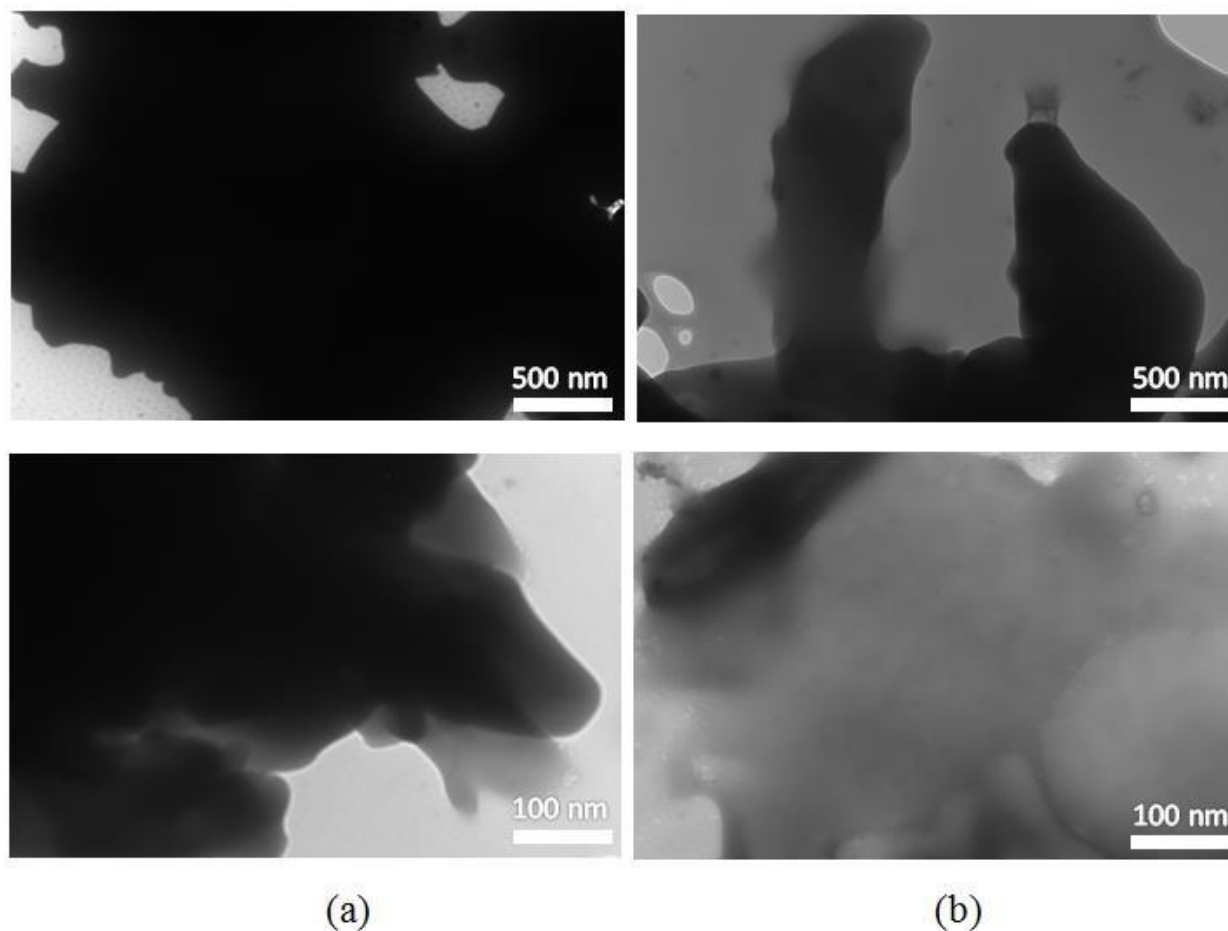


Figure 5: TEM Images for Dispersion of graphene in (a) PEI/G_{0.5} and (b) PEI/G_{0.1} composite.

Potentiodynamic and Impedance Measurements

Cyclic voltammeter and impedance spectroscopy were utilized to study the electrochemical behaviors of bare as well as PEI and PEI/G coated SS304 substrates. All measurements were conducted in a temperature controlled 3.5% NaCl solution. The cyclic voltammeter technique was carried out to generate the Tafel plots for bare and coated SS304 substrates as depicted in (Figure 6). Moreover, valuable corrosion parameters were extracted

from Tafel plots such as corrosion currents and corrosion potentials and corrosion rates. The corrosion currents were reported as the intersection between the linear portions of the anodic and the cathodic curves in the Tafel plots. The variations in the corrosion parameters, which are reported in (Table 1), may help understanding the influences of the different coatings on the corrosion behaviors of bare

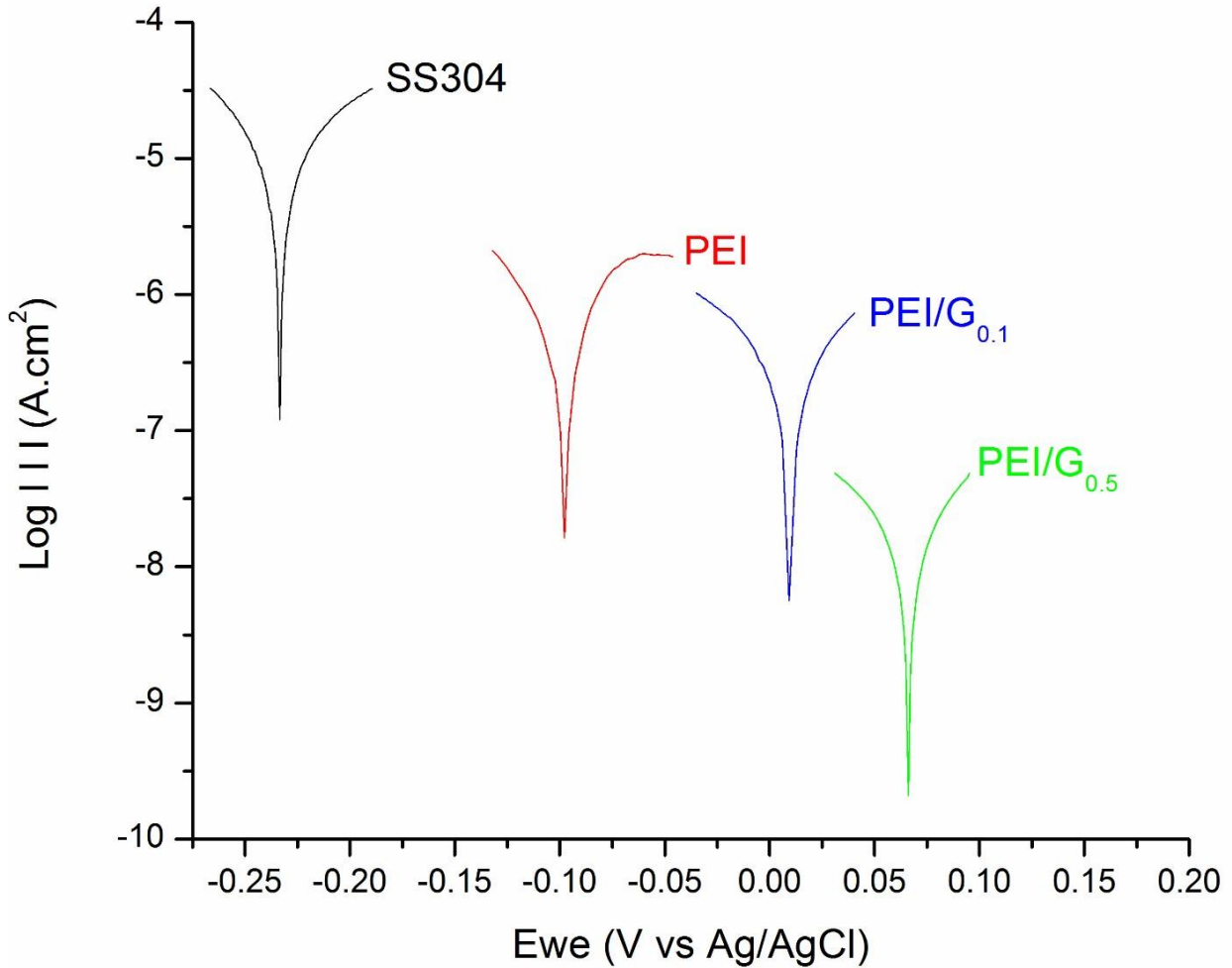


Figure 6: Tafel plots for Bare SS304, PEI, PEI/G_{0.1} and PEI/G_{0.5} coated SS304 substrates.

SS304. From the parameters reported in (Table 1), it can be observed that a positive shift E_{corr} plus a drop in I_{corr} and R_{corr} were encountered after coating SS304 with PEI, which are signs of reduction in the corrosion rate. Furthermore, the intensities of these shifts in the corrosion parameters were more pronounced after the incorporation of graphene, which are indications of further protection from corrosion. Finally, the I_{corr} magnitudes were used to compute the protection efficiencies (P_{EF}) of the different coatings, which are also reported in (Table 1), using (2), where I_{corr} and I_{corr}° represent the corrosion current of coated and bare SS304 substrates, respectively.

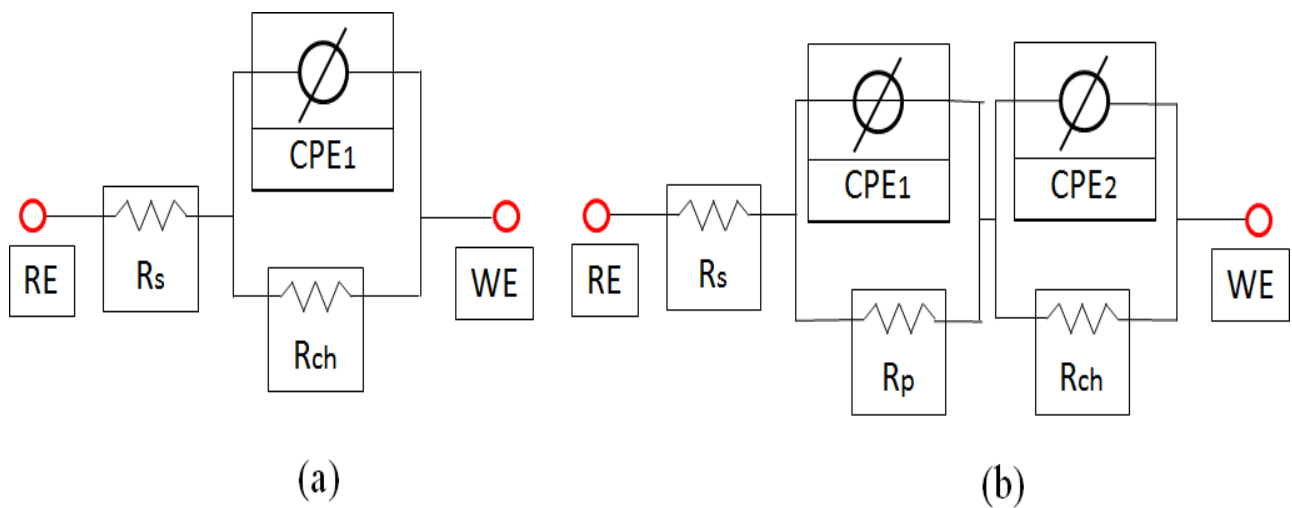


Figure 7: Equivalent circuits to model impedance behavior of (a) Bare SS304, (b) PEI, PEI/G_{0.1} and PEI/G_{0.5} coated SS304 substrates.

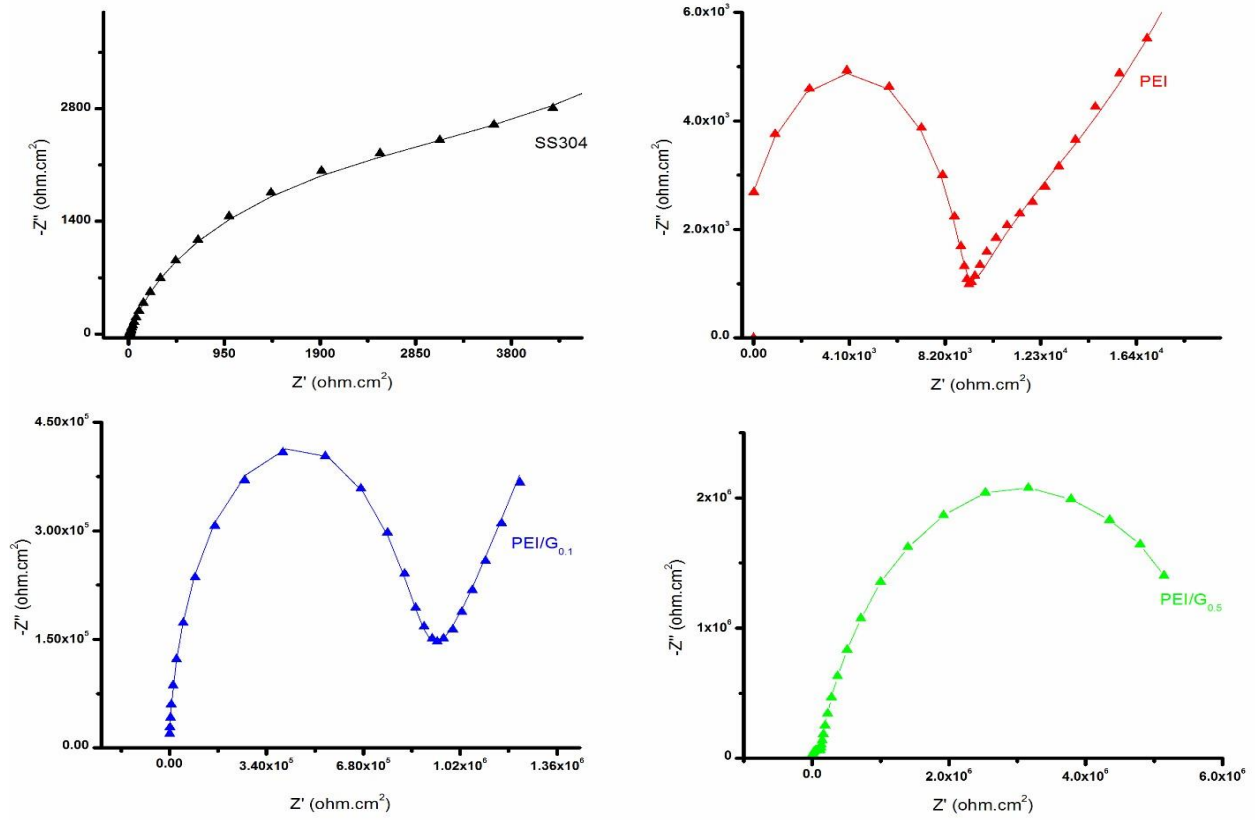


Figure 8: Nyquist plots for Bare SS304, PEI, PEI/G_{0.1} and PEI/G_{0.5} coated SS304 substrates.

$$P [\%] = \left(1 - \frac{I_{corr}^{EF}}{I_{corr}^{\circ}}\right) \times 100 \quad (2)$$

Table 1: Corrosion parameters from cyclic voltammetry measurements for Bare SS304, PEI, PEI/G_{0.1} and PEI/G_{0.5} coated SS304 substrates in 3.5% NaCl Solution.

Sample	Corrosion Parameters Extracted From Tafel Plots			
	E _{corr} [mV vs Ag/AgCl]	I _{corr} [μA/cm ²]	R _{corr} [MPY]	P _{EF} [%]
SS304	-238.2	1.3	0.49	-
PEI	-100.1	0.037	0.017	96.8

Sample	Corrosion Parameters Extracted From Tafel Plots			
	E_{corr} [mV vs Ag/AgCl]	I_{corr} [$\mu\text{A}/\text{cm}^2$]	R_{corr} [MPY]	P_{EF} [%]
PEI/G _{0.1}	17.3	0.026	0.011	97.9
PEI/G _{0.5}	65.85	0.0048	0.0005	99.6

EIS had also been utilized to examine the electrochemical activities of the bare and coated SS304 substrates. Here, a complex form of resistance known as impedance is observed, when an alternative current is forced through a circuit that might contain different elements such as resistors and capacitors. This approach was used to study the impedance behaviors of bare and coated SS304 substrates. Furthermore, the depicted equivalent circuits in (Figure 7) were used to model the impedance behaviors of the bare and coated metal substrates, where R_s , R_p and R_{ch} represent the 3.5% NaCl solution, coating and charge transfer resistances, respectively and CPE is the constant phase element. From the fitting, the magnitudes of the various elements in the equivalent circuits were evaluated and the variation in impedance activities on the bare and coated substrates were assessed.

(Figure 8), depicts the impedance behaviors of the different samples and in general, an increase in the size of the semi-circle represents an enhancement in corrosion protection. Moreover, an increase in the charger transfer resistance represents a slower corrosion rate. Since the fitting data fits well to the raw impedance data as illustrated in (Figure 8), the charge transfer resistances can be computed using the equivalent circuits depicted in (Figure 7) and the charge transfer resistances for bare, PEI, PEI/G_{0.1}, PEI/G_{0.5} coated SS304 substrates are 4002, 9501, 8.3 x 10⁵ and 5.8 x 10⁶ $\Omega\cdot\text{cm}^2$, respectively.

4. Conclusion

PEI/G composites were prepared by in situ polymerization and thermally cured on a SS304 substrate to investigate the influence of the incorporation of graphene on the corrosion protection property of PEI coated SS304 substrates. Electrochemical measurements such as cyclic voltammetry and impedance spectroscopy were utilized to evaluate the corrosion behaviors of the PEI/G coated meal substrates. The degree of dispersion of the graphene sheets

in the polymeric matrices was captured using SEM and TEM at low and high magnifications. In addition, the interface adhesion between the prepared coating and the metal substrates were evaluated according to ASTM D3359 standard.

The reported results demonstrate that PEI may protect SS304 substrate from corrosion in a 3.5% NaCl solution. Furthermore, the corrosion protection property of PEI can be enhanced by the incorporation of graphene. Finally it was interesting to observe that increasing the load of graphene may results in loss of interface adhesion between the PEI/G composites and the SS304 substrate.

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REFERENCES

- ASTM International (2010). Standard Practice for Calculation of Corrosion Rates and Related Information from Electrochemical Measurements. West Conshohocken, PA. 10.1520/G0102-89R10
- ASTM International (2009). Standard Test Methods for Measuring Adhesion by Tape Test. West Conshohocken, PA. 10.1520/D3359-09E02
- Cecchetto, L., Delabouglise, D., Petit, J. P. (2007). On the mechanism of the anodic protection of aluminium alloy AA5182 by emeraldine base coatings: Evidences of a galvanic coupling. *Electrochimica Acta*, 52(11), 3485-3492.
- Chang, C. H., Huang, T. C., Peng, C. W., Yeh, T. C., Lu, H. I., Hung, W. I., Weng, C. J., Yang, T. I., Yeh, J. M. (2012). Novel anticorrosion coatings prepared from polyaniline/graphene composites. *Carbon*, 50(14), 5044-5051.
- Chang, K. C., Hsu, C. H., Lu, H. I., Ji, W. F., Chang, C. H., Li, W. Y., Chuang, T. L., Yeh, J. M., Liu, W. R. (2014). Advanced anticorrosive coatings prepared from electroactive

- Polyimide/graphene nanocomposites with synergistic effects of redox catalytic capability and gas barrier properties. *Express Polymer Letters*, 8(4), 243-255.
- Chang, K. C., Hsu, M. H., Lu, H. I., Lai, M. C., Liu, P. J., Hsu, C. H., Ji, W. F., Chuang, T. L., Wei, Y., Yeh, J. M., Liu, W. R. (2014). Room-temperature cured hydrophobic epoxy/graphene composites as corrosion inhibitor for cold-rolled steel. *Carbon*, 66, 144-153.
- Crosby, A. J., Lee, J. (2007). Polymer nanocomposites: The “nano” effect on mechanical properties. *Polym. Rev.*, 47(2), 217-229.
- Guo, S. F., Zhang, H. J., Liu, Z., Chen, W., Xie, S. F. (2012). Corrosion resistances of amorphous and crystalline Zr-based alloys in simulated seawater. *Electrochemistry Communications*, 24, 39-42.
- Kang, G., Kan, Q., Zhang, J., Sun, Y. (2005). Time-dependent ratchetting experiments of SS304 stainless steel. *International Journal of Plasticity*, 22(5), 858-894.
- Moretti, G., Guidi, F., Grion, G. (2004). Tryptamine as a green iron corrosion inhibitor in 0.5 M deaerated sulphuric acid. *Corrosion Science*, 46(2), 387-403.
- Ojha, O., Anjaneyulu, O., Ganguli, A. K. (2014). Graphene-based hybrid materials: synthetic approaches and properties. *Current Science*, 107 (3), 397-418.
- Potts, J. R., Shankar, O., Du, L., Ruoff, R. S. (2012). Processing-morphology-property relationships and composite theory analysis of reduced graphene oxide/natural rubber nanocomposites. *Macromolecules*, 45(15), 6045-6055.
- Prasai, D., Tuberquia, J. C., Harl, R. R., Jennings, G. K., Bolotin, K. I. (2012). Graphene: corrosion-inhibiting coating. *ACS Nano*, 6(2), 1102-1108.
- Roy, D., Simon, G. P., Forsyth, M., Mardel, J. (2002). Towards a better understanding of the cathodic disbondment performance of polyethylene coatings on steel. *Advances in*

Polymer Technology, 21(1), 44-58.

Shen, G. X., Chen, Y. C., Lin, C. J. (2005). Corrosion protection of 316 L stainless steel by a TiO₂ nanoparticle coating prepared by sol-gel method. *Thin Solid Films*, 489(1-2), 130-136.

Singh, B. P., Jena, B. K., Bhattacharjee, S., Besra, L. (2013). Development of oxidation and corrosion resistance hydrophobic graphene oxide-polymer composite coating on copper. *Surf. Coat. Tech*, 232, 475-481.

The International Nickel Company Inc. (1963). *Corrosion Resistance of the Austenitic chromium-nickel Stainless steels in chemical environments*. New York.

Xu, Z., Buehler, M. J. (2010). Geometry controls conformation of graphene sheets: Membranes, ribbons, and scrolls. *ACS Nano*, 4(7), 3869-3876.