Corrosion Study of Graphene Coatings on Carbon Steels

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ABSTRACT
The functionalized graphene with epoxy was applied on carbon steel pipes ASTM A53 grade B. The corrosion properties of coated and uncoated carbon steels were evaluated using a three-electrode cell system in NaCl solution at room temperature. The findings suggest a shift of corrosion potential value, a decrease of corrosion current density and corrosion rate, and an increase of inhibition efficiency by applying graphene-epoxy coatings on the substrate. This is attributed to the role of functionalized graphene networks that hinders chloride ions penetrate into the carbon steel surface.

Keywords: *Graphene, Epoxy, Composite Coating, Corrosion, Carbon Steel.*

1. INTRODUCTION

The most frequently used material for process piping in oil and gas industry is carbon steel pipe. The advantages of using carbon steel pipe are wide availability, high strength, and a large array of connection possibilities. The pipe application must consider some operational conditions that include corrosion [1], [2]. Corrosion-resistant alloys can be used in place of carbon steel to alleviate replacement costs. However, due to their production cost, these alloys are limited in use [3].

Corrosion inhibitors are one of the properly applied, most efficient, and inexpensive methods of corrosion prevention to protect the inner wall of the petroleum pipeline from corrosive materials and temperatures. In the past, pre-treatments based on chromium have been used widely, with reasonable results since it can serve as an inhibitor of both cathodic (Cr^{3+}) and anodic (Cr^{6+}). They facilitate adhesion to paint, prevent corrosion, and are cost-effective [4]. However, its use has been limited as a result of the adverse effects of chromium (VI) on human health and the environment [5]. Composite coatings of Ni-P/SiC also display strong resistance to wear and corrosion [6], [7]. However, both materials, such as chemical vapor deposition, are costly and need special implementation techniques. Therefore, they do not satisfy the practicality.

Recently, because it has extremely high electrical and thermal conductivity, power, and ductility, graphene has attracted considerable interest [8], [9]. Furthermore, graphene has been shown to be chemically inert and impermeable to hostile acids, such as HF [10], [11]. Graphene's high surface area and hydrophobic nature played crucial roles in preventing corrosion [12]. The addition of graphene to corrosion inhibitors such as hydroxyls, epoxides, carboxyl's, amine groups, etc. has greatly improved the efficiency of the coatings against corrosion [13]. Due to its non-toxic and low-cost polymer, epoxy is selected as the matrix in this work. In addition, because of good corrosion resistance, good thermal stability, high tensile strength, and prominent interfacial adhesion, epoxy is typically used as coating materials against corrosion [14].

Thus, this study investigates the influence of graphene-epoxy coating on carbon steel substrate. Carbon steel pipes ASTM A53 Grade B will be used as the substrate as it has been utilized extensively for pressurized equipment and pipes below 350°C. Using the bath process, the functionalized graphene-epoxy coatings is prepared. Potentiodynamic polarization is used to examine the corrosion properties, i.e., corrosion potentials, corrosion current densities, corrosion rate, and inhibition efficiency.

2. METHOD AND MATERIALS

All processes of substrate coating on substrates were carried out in PEM Akamigas laboratory. Graphene nanoplatelets from XFNANO LLC were used as a raw material in this work. Additionally, Araldite 506 epoxy resin from Sigma Aldrich had been used as the polymer matrix. As substrates, carbon steel pipes ASTM A53 grade B with the inside diameter of 26.6 mm were prepared. The substrate density was 10.0 g/cm^3.

The substrates were treated with sandpaper, washed with ethanol and demineralized water, and dried using air flow to eliminate the residual impurities using air flow. Graphene nanoplatelets were initially spread into 50 ml of pure ethanol for the functionalization of graphene-epoxy coatings and stirred for 30 minutes. The one-hour sonification was added to obtain a uniform graphene/ethanol mixture solution. Afterwards, 25 g epoxy mixed with the hardener was supplemented into the solution and subsequently the one-hour sonification was again applied to obtain a uniform solution of graphene and epoxy mixture. The final graphene content in graphene and epoxy mixture was 2.0 wt%. A brush was used to paint uniform solution of graphene/epoxy on each cleaned substrate. Further to this step, the composite coatings were elevated for 24 hours at 60°C and then cured for 1 hour and 30 minutes at 100°C. The coated samples were then allowed to cool at the ambient temperature for 6 hours.

Potentiodynamic polarization corrosion experiments using a three-electrode cell system were performed. The carbon steel substrate with the exposed surface area of 0.80 cm^2 was used as a working electrode, the graphite rod was used as a counter electrode, and the calomel saturated electrode was used as a reference electrode. NaCl developed by Merck was diluted using double distilled water to create a 3.5% NaCl solution working as a test solution. After a steady state condition was reached at open circuit potential, Tafel scans were conducted (OCP). The scans were ranged from -0.05 V to +0.05 V at a scan rate of 0.50 mV/s. The corrosion potential (E_{corr}) and corrosion current density (i_{corr}) were determined from Tafel plots of potential *E* as a function of log current *I*. Using equation (1), the corrosion rate of the carbon steel substrate was calculated [15].

$$C = \frac{K \times i_{corr} \times EW}{\rho} \quad (1)$$

where C is the corrosion rate in mmpy, K is 3.27×10^{-3} mm g/µA cm yr, i_{corr} is the corrosion current density in µA/cm^2, EW is the equivalent weight of substrate which is considered dimensionless, and ρ is the density of substrate in g/cm^3. Afterwards inhibition efficiency (IE) was measured from the corrosion current density values of the uncoated and coated graphene samples as follows [16]:

$$IE = \frac{i^0_{corr} - i_{corr}}{i^0_{corr}} \times 100 \quad (2)$$

where i^0_{corr} is the corrosion current density of uncoated specimen in µA/cm^2 and i_{corr} is the corrosion current density of coated specimen in µA/cm^2.

3. RESULT AND DISCUSSION

Tafel curves of the carbon steel substrates in the absence and presence of graphene-epoxy coatings are shown in Figure 1. The corrosion potential (E_{corr}) that illustrate the susceptibility of the coatings on the corrosive chloride ion medium [17] is observed from these Tafel curves. By applying a graphene-epoxy coating on the substrate, the corrosion potential was proven to increase towards positive values. The larger the corrosion potential, the greater the corrosion resistance of the coating to the corrosive Cl^- ion environment [17], [18].

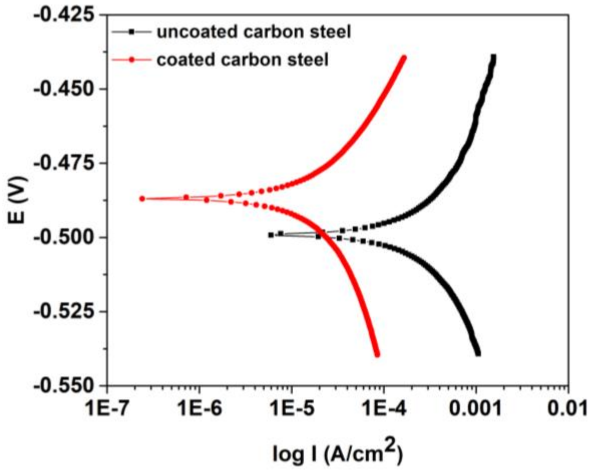

Figure 1 Tafel curves for the tube carbon steels in the absence and presence of varied graphene contents in the graphene-epoxy coatings in 3.5% NaCl solution at room temperature

The parameters shown in , i.e. anodic slope, cathodic slope, corrosion current density, corrosion rates, and inhibition efficiency, will more clearly demonstrate the dependence of the coating presence on corrosion behaviors. Polarization studies found that graphene in the graphene-epoxy composite behaved as strong corrosion inhibitors and the nature of anodic and cathodic Tafel polarization curves was affected by their existence. The drop in corrosion current density values in the presence of graphene in the graphene-epoxy composite suggested that the active sites on the substrate surface were blocked successfully [5], [19], [20].

Table 1. Various parameters measured from potentiodynamic polarization for substrates in the absence and presence of the graphene-epoxy coatings

Graphene content (%)	β_a (mV/dec)	β_c (mV/dec)	I_{corr} (μA/cm^2)	E_{corr} (V)	C (mmpy)	IE (%)
0.0	75.63	158.23	2.404×10^{-04}	-0.500	2.7933	0.00
2.0	113.36	375.07	1.469×10^{-05}	-0.486	0.1706	93.89

The corrosion rates are directly proportional to the corrosion current densities of the samples, as given in Eq. (1). The corrosion rate was 2.7933 mmpy in the absence of graphene-epoxy composite, which was greater than that in the presence of graphene-epoxy composite. The corrosion rate was reduced by a factor of 10. It can also be shown that for coated samples the inhibition efficiencies have been improved. These results correspond to a more improved barrier from acid attacks offered by graphene-epoxy coatings. Moreover, graphene atoms functionalized with epoxy adsorb more closely to the carbon steel surface and are impermeable to the corrosion species [17], [20].

4. CONCLUSION

The research has been performed to investigate the influence of graphene-epoxy coatings on the corrosion properties of carbon steel in NaCl solution at room temperature. Potentiodynamic polarization measurements have shown that graphene-epoxy coatings added on the carbon steel substrate work effectively against. The dependency of corrosion potential on graphene-epoxy coating application has been observed. In addition, the decrease in corrosion current density and corrosion rates suggest that the active sites on the substrate surface were successfully blocked by the presence of graphene in the graphene-epoxy composite. It can also be shown that the inhibition efficiencies have been increased for coated samples.

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REFERENCES

[1] M. Stewart, “3 - Material requirements: Piping materials,” in Surface Production Operations, M. Stewart, Ed. Boston: Gulf Professional Publishing, 2016, pp. 159–192.

[2] J. Lee, S. Han, K. Kim, H. Kim, and U. Lee, “Failure analysis of carbon steel pipes used for underground condensate pipeline in the power station,” Eng. Fail. Anal., vol. 34, pp. 300–307, Dec. 2013, doi: 10.1016/j.engfailanal.2013.08.005.

[3] R. Albert, L. W. McKeen, and J. Hofmans, “Corrosion Testing Of Fluorocoatings For Oil/Gas Production Tubing .” Mar. 16, 2008.

[4] P. D. Deck, M. Moon, and R. J. Sujdak, “Investigation of fluoacid based conversion coatings on aluminum,” Prog. Org. Coatings, vol. 34, no. 1–4, pp. 39–48, Jul. 1997, doi: 10.1016/S0300-9440(98)00017-4.

[5] K. S. Aneja, S. Bohm, A. S. Khanna, and H. L. M. Bohm, “Graphene based anticorrosive coatings for Cr(vi) replacement,” Nanoscale, vol. 7, no. 42, pp. 17879–17888, 2015, doi: 10.1039/C5NR04702A.

[6] G. R. Yang, W. M. Song, X. M. Sun, Y. Ma, and Y. Hao, “The Corrosion Behavior of Ni-P/SiC Composite Coating,” Adv. Mater. Res., vol. 291–294, pp. 215–218, Jul. 2011, doi: 10.4028/www.scientific.net/AMR.291-294.215.

[7] G. R. Yang, W. M. Song, X. M. Sun, Y. Ma, J. J. Lu, and Y. Hao, “The Wear Behavior of Electroless Ni-P/SiC Composite Coating,” Adv. Mater. Res., vol. 239–242, pp. 954–957, May 2011, doi: 10.4028/www.scientific.net/AMR.239-242.954.

[8] K. S. Novoselov et al., “Electric field effect in atomically thin carbon films.,” Science, vol. 306, no. 5696, pp. 666–9, Oct. 2004, doi: 10.1126/science.1102896.

[9] F. Bonaccorso et al., “Graphene, related two-dimensional crystals, and hybrid systems for energy conversion and storage,” Science (80-.)., vol. 347, no. 6217, p. 1246501, Jan. 2015, doi: 10.1126/science.1246501.

[10] E. Stolyarova et al., “Observation of Graphene Bubbles and Effective Mass Transport under Graphene Films,” Nano Lett., vol. 9, no. 1, pp. 332–337, Jan. 2009, doi: 10.1021/nl803087x.

[11] J. S. Bunch et al., “Impermeable atomic membranes from graphene sheets.,” Nano Lett., vol. 8, no. 8, pp. 2458–2462, Aug. 2008, doi: 10.1021/nl801457b.

[12] S. Böhm, “Graphene against corrosion,” Nat. Nanotechnol., vol. 9, no. 10, pp. 741–742, 2014, doi: 10.1038/nnano.2014.220.

[13] V. Georgakilas et al., “Functionalization of Graphene: Covalent and Non-Covalent Approaches, Derivatives and Applications,” Chem.

Rev., vol. 112, no. 11, pp. 6156–6214, Nov. 2012, doi: 10.1021/cr3000412.

[14] Y. Ziat, M. Hammi, Z. Zarhri, and C. Laghlimi, "Epoxy coating modified with graphene: A promising composite against corrosion behavior of copper surface in marine media," J. Alloys Compd., vol. 820, p. 153380, 2020, doi: https://doi.org/10.1016/j.jallcom.2019.153380.

[15] ASTM, "Standard Practice for Calculation of Corrosion Rates and Related Information from Electrochemical Measurements," West Conshohocken, PA, USA, 1994.

[16] C. Verma, M. Quraishi, E. Ebenso, and M. Reddy, "Electrochemical and Thermodynamic Investigation of Nitrofurantoin as Effective Corrosion Inhibitor for Mild Steel in 1M Hydrochloric Acid Solution," Int. J. Electrochem. Sci., vol. 8, pp. 12894–12906, 2013.

[17] A. Gupta and C. Srivastava, "Enhanced corrosion resistance by SnCu-graphene oxide composite coatings," Thin Solid Films, vol. 669, pp. 85–95, Jan. 2019, doi: 10.1016/j.tsf.2018.10.036.

[18] R. K. Singh Raman and A. Tiwari, "Graphene: The Thinnest Known Coating for Corrosion Protection," JOM, vol. 66, no. 4, pp. 637–642, 2014, doi: 10.1007/s11837-014-0921-3.

[19] K. Haruna, T. A. Saleh, I. B. Obot, and S. A. Umoren, "Cyclodextrin-based functionalized graphene oxide as an effective corrosion inhibitor for carbon steel in acidic environment," Prog. Org. Coatings, vol. 128, pp. 157–167, 2019, doi: https://doi.org/10.1016/j.porgcoat.2018.11.005.

[20] M. A. Krishnan et al., "Graphene-based anticorrosive coatings for copper," RSC Adv., vol. 8, no. 1, pp. 499–507, 2018, doi: 10.1039/C7RA10167H.