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Effect of reduced graphene oxide nanoparticles as anticorrosion material on mild steel substrate

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Abstract. Reduced graphene oxide(rGO) has a lot of potential in the area of corrosion control of metals, because of its excellent barrier properties, dispersion capabilities, and impermeability. The current work hires on the corrosion resistance action of reduced graphene oxide(rGO) as an inhibitor for mild steel in simulated concrete pore solution. Here, three different nano rGO contained epoxy coatings were prepared by varying the percentage of rGO. The anticorrosion behaviour of rGO integrated epoxy composite coating was evaluated using open circuit potential and polarization studies. The results indicated that rGO nanoparticles were properly distributed in the epoxy coating and showed excellent barrier properties. Moreover, anti-corrosion processes for composite coatings improved by the addition of various percentages of rGO were apparently hypothesized, implying that epoxy coating containing 1.0 wt.% rGO showed better corrosion resistant behaviour in concrete pore solution medium containing 0.5M NaCl solution.

Keywords: Reduced graphene oxide; Epoxy-Nano composite coating; Corrosion; Mild steel; Simulated concrete pore solution.

1. Introduction

Corrosion is considered to be one of the severe reasons for the deterioration of structures. It produces significant losses and is seen as a critical global issue for metallic products. Mild steel (MS) is one of the most essential metals used in construction areas and equipment's because to its excellent engineering properties and inexpensive, however it is highly corrosive. As a result, corrosion prevention for MS structures is a significant issue [1,2]. Several approaches have been proposed for the corrosion protection of metals including several surface treatments, use of corrosion inhibitors, application of coatings etc. [3,4]. From these methods, providing organic coating seems to be more reliable and effective solution for protection action for metals. Epoxy based organic coatings provide good physical protection against the penetration of corrosive agents and it also have greater improvements in durability aspects [5,6]. The effectiveness of this type of coating are always influenced by the process of coating, the nature of the corrosion products and the compatibility of organic materials [7]. Several studies are conducted to overcome the drawbacks of pure epoxy-based coatings. Researchers had found that incorporation of nanomaterials into the epoxy inhibits corrosion of metals predominantly [8,9]. Because of its superior anticorrosion properties, graphene modified nanocomposite coatings have gotten a lot of attention in recent years. Reduced graphene oxide, or rGO, is a form of synthetically produced graphene with unique features like high thermal conductivity, high chemical impermeability, bigger surface area, high dispersion, and exceptional electron mobility. On the other hand, the capacity of rGO in the area of



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corrosion control, has yet to be properly exploited. [10,11]. It is indicated that several reduced graphene modified coatings had proved better anticorrosion behaviour for various metals in 3.5 wt. % of NaCl medium [12]. Lijuan Zhu et al [13] also described the corrosion mechanism of rGO composite coating and its anticorrosion behaviour under high salinity and temperature conditions. In an alkaline pH of 11, an electrode was developed via surface electrochemical/ chemical coating with rGO over a bare metal electrode [14]. The rate of corrosion was also affected by variations in pH. By the attack of certain chemicals that may lower the pH of the concrete pore solution and as a result, the metals would be vulnerable to various attacks. The surface of the steel depassivates as pH of concrete pore solution drops and corrosion commences [15]. Studies in simulated concrete solutions have been done to get additional understanding into the mechanism by which steel corrosion in salt-contaminated concrete occurs [16]. Studies indicated that with addition of certain inhibitors to such concrete pore solution mediums effectively slows the corrosion rate of metal substrates [17,18]. Moreover, further research into the effects of rGO on polymer composites in a concrete environment is required. The anticorrosion behaviour of rGO coatings in pore solutions with fluctuating pH is rarely mentioned.

This study contributes a solution for corrosion affected problems and the findings are crucial in promoting the usage of reduced graphene-epoxy coatings in a variety of building applications. Work includes firstly rGO nano particles were synthesized from graphite powder by modified Hummer's method and then rGO-EP composite coatings were prepared to investigate the impact of rGO on the corrosion resistant behaviour of mild steel. Using open circuit potential (OCP) and potentiodynamic polarization methods, the corrosion inhibition behaviour of epoxy (EP) and hybrid EP coatings including varying percentages of rGO in concrete pore solution was compared.

2. Experimental Section

2.1. Materials and Solution

Graphite powder (325 mesh), Epoxy resin (bisphenol A diglycidal ether) and hardener (Triethylenetetramine TETA) were purchased from Sigma Aldrich. The mild steels ($3 \times 1 \times 0.3$ cm) were polished by 800 grit emery sheets were taken for the corrosion study.

2.2. Synthesis of reduced graphene oxide (rGO)

The Reduced graphene oxide (rGO) was developed via modified Hummer's method utilizing graphite powder [19]. In the initial stage we are converting graphite powder to graphene oxide (GO) and then to rGO. Firstly, introduce 2.5g of graphite powder gently to 60 ml H₂SO₄ (98%) and mixed repeatedly in an ice bath for 20min. The sample was kept in an ice bath in order to maintain the temperature under 5°C. Further the beaker was placed with 1.25 g of KNO₃ and stirred for 25 minutes. Once the graphite has been thoroughly mixed, pour 7.5g of KMnO₄ dropwise into the solution and mixed well for a period of 1 hr at 5°C. After that the beaker was taken out from the ice bath and agitated for 1 hour at 35°C until a thick dark green paste was achieved. Add 300mL of deionized water slowly into the green paste, accompanied by dropwise inclusion of 50 mL of 30 percent H₂O₂ causes rise in temperature to 98 °C. This process may take approximately 1hr and the resultant mixture turned into a vivid yellowish-brown colour. After obtaining a homogenous mix, it was strained through Whatman filter paper of pore size 125 mm. Then the permeate was cleaned with deionized water for certain period. It was mixed using deionized water before being sonicated for an hour, prior to that centrifuged at 7000 RPM (rpm). The precipitant was separated, and the graphene oxide that had settled was transferred into a clean beaker, which was placed in an oven for 24 hours at 60 degrees Celsius in order to make GO powder.

Second stage involves conversion GO to rGO; the procedure is as follows. Take about 100mg of GO powder and dissolved it with 150mL deionized water. Sonicate the mixture for 30 min. Introduce 1 g of ascorbic acid into the solution and mixed it well for 10-15 minutes. In order to adjust the pH of the solution to 12, introduce 25 percent ammonia dropwise and further sonicated for 20 minutes. The temperature of the solution was elevated to 85 °C at this point and its colour was shifted from brown to brownish-black. After homogenising the mixture for 1.5 hours, the colour was turned to dark black,

indicating that GO had been converted to rGO. The final composition was then purified and rinsed with deionized water for multiple times. At last, rGO was obtained after drying the rGO solution by keeping it in an oven for one day at 60°C.

2.3. Exposure Solution

Experiments were carried out at room temperature. Simulated concrete pore solution containing estimated composition of 0.3M potassium hydroxide (KOH), 0.1M sodium hydroxide (NaOH), 0.03M $\text{Ca}(\text{OH})_2$ and 0.002M CaSO_4 with a pH of 12.5 was prepared as the electrolyte. In order to simulate an exposure similar to seawater, chloride was introduced as NaCl at concentrations of 0.5M [20].

2.4. Preparation of rGO-Epoxy Nano composite Coating

Mild steel samples were cut into a dimension of 3cm x 1cm. The samples were prepared by polishing the surface with 800 grits of emery paper. Further cleaned with ethanol to remove the inorganic matters and kept it for drying at room temperature. A well-specified area of 1cm x 1cm was selected for the coating area.

rGO-Epoxy composite coating was prepared according to the following procedure as depicted Fig1. rGO nanoparticles were dispersed ultrasonically for 15-20 minutes at room temperature after being put directly into ethanol at a concentration of 30ml/g. The dispersed rGO solution was then diluted with 30mg epoxy resin and mechanically stirred for 12 hours at 2000 rpm with in a temperature of 70°C and there by removed the ethanol. Later, stoichiometric volume of hardener was introduced to the rGO suspension (weight ratio of hardener to epoxy was taken as 58:100) and agitated for another 10 minutes manually. The epoxy coating with various rGO compositions (0.5%, 1 %, and 2 %) was painted over the metal surface and allowed to cure at room temperature for 24 hours before being placed in a 60°C oven for 12 hours. Diagrammatic representation for the preparation procedure of rGO composite coating is shown in Figure1.

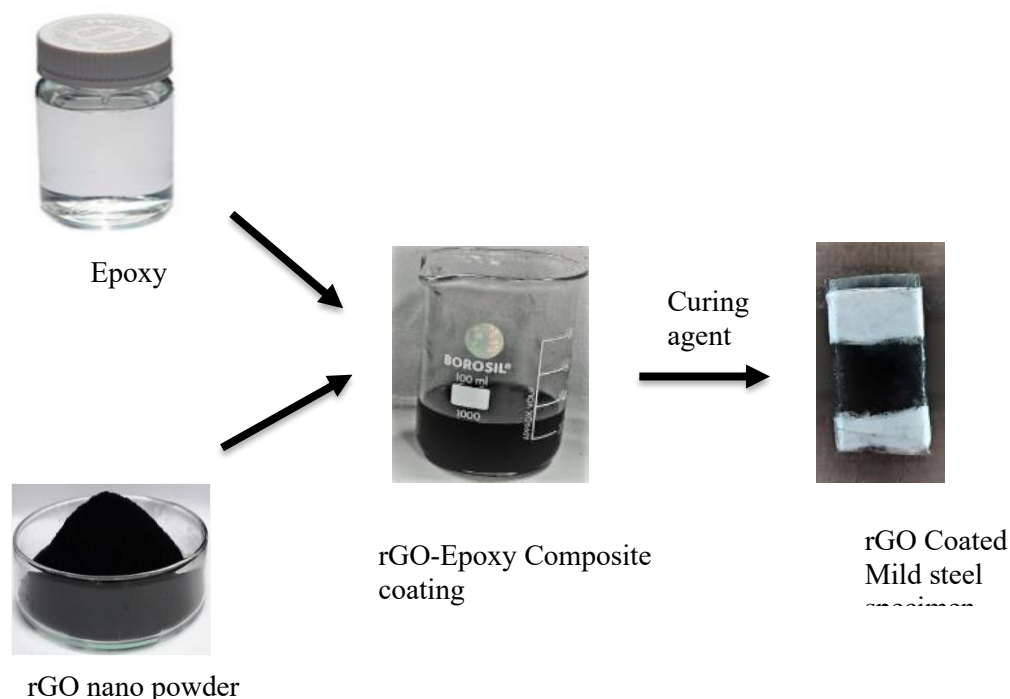


Figure 1. Diagrammatic representation for the preparation procedure of rGO-epoxy composite Coatings.

2.5. Electrochemical studies

The anticorrosion performance of coated mild steel samples was performed using electrochemical studies. The analysis consists of open circuit potential test and polarization measurements. The electrochemical measurement was conducted by immersing the rGO coated samples in concrete pore solution containing 0.5M NaCl medium through a potentiostat with an ordinary three-electrode system comprised of a platinum metal as counter electrode, saturated calomel electrode (SCE) as a reference electrode and coated sample as working electrode. The test was executed for a selected area of 1 cm². All measurements were carried out in a CPS medium on a Bio-logic (SP300) potentiostat workstation. Samples were tested after reaching a stabilized potential (30 min). At a scan rate of 1 mV/s, Tafel polarization was used to estimate the corrosion measurements with in the interval of -0.25 V to 0.25 V (vs. OCP). The test setup is shown in Figure.2.



Figure 2. Electrochemical test setup.

3. Results and Discussion

3.1. OCP Measurements

The Open circuit potential (OCP) measurements of coated samples after immersing in concrete pore solution containing 0.5M NaCl for a certain period of time (1800 sec) as shown in Figure 3. It was noted that the potential values move towards higher regions with increase in percentage of rGO content. Compare to pure epoxy coated substrate rGO coated sample displays greater potential values, indicating proper dispersion of rGO in the epoxy matrix. At the same time, with increase in immersion period, there occurs a drop in potential values and reaches almost constant values after 15 min duration. This drop in values indicates the activation of chloride ions in the electrolyte and it leads to distortion of mild steel under pH of 11.5. The shift of OCP value towards more negative region indicates that chances to corrosion was more. While comparing OCP values, it's worth noting that epoxy composite coating with 1.0 wt.% rGO indicates less shift of OCP (-0.162V to -0.194V) value towards negative side, indicate that it creates better barrier nature in the epoxy coating, hence protect the MS substrate from exterior corrosive mediums.

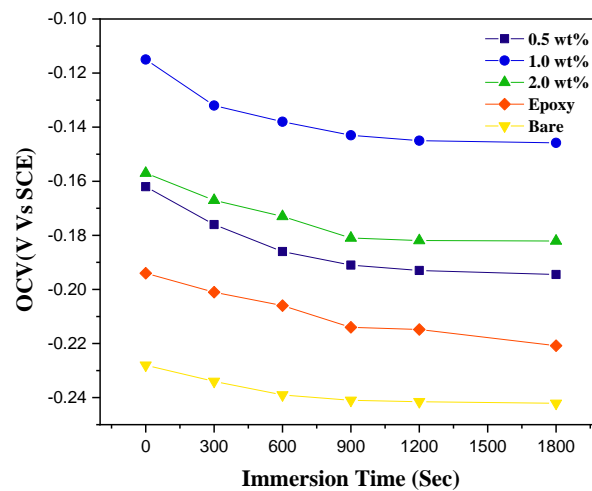


Figure 3. OCP values for coated samples in SCP containing 0.5M NaCl solution at different immersion periods.

3.2. Tafel Analysis

The anticorrosion behaviour of different contents of rGO epoxy composite coatings on mild steel specimens were analysed and compared with pure epoxy coatings as well as bare samples after immersed in concrete pore solution (CPS) containing 0.5M NaCl medium for 24 hrs duration. Tafel plots for the rGO/EP composite coatings were depicted in Figure 4. It was clear that the incorporation of rGO resulted in a considerable reduction in corrosion current (I_{corr}) and in corrosion potential (E_{corr}) indicates a significant change towards positive direction. This indicated that prior to the application of coatings, corrosion susceptibility of the sample surface has been minimized. Table 1 shows the assessed electrochemical parameters, such as corrosion potential, corrosion current density, anodic tafel slopes, cathodic Tafel slopes, corrosion rate and efficiency. From the literatures it was known that greater E_{corr} and a lower I_{corr} are often thought to indicate better corrosion resistance [21]. The potential values and slopes (E_{corr} , I_{corr} , β_c and β_a) were obtained by extrapolating tafel curves using an EC lab Software. Rate of corrosion can be measured from equation 1.

$$CR = \frac{K i_{corr} E_w}{d} \quad (1)$$

Where K denotes the corrosion rate constant, I_{corr} represents corrosion current density obtained by tafel extrapolation, E_w represents equivalent weight of mild steel (55.85 g/mol), ρ represents density of steel (7.85 g/cm³).

Polarization resistance can be calculated according to equation 2.

$$R_p = \frac{\beta_a \beta_c}{2.3 i_{corr} (\beta_a + \beta_c)} \quad (2)$$

In this case, the corrosion inhibition efficiency ($\eta\%$) of mild steel substrate was estimated using equation 3.

$$\eta\% = \frac{icorr(bare) - icorr(coated)}{icorr(bare)} \times 100 \quad (3)$$

According to both polarization curves and values given in Figure 4 and Table 1, it was revealed that rGO coated specimens increased its corrosion resistance and the films gained significant barrier characteristics. Evidently the current density (I_{corr}) of the rGO coated sample was 1.59×10^{-6} A/cm², it was significantly lower than the bare sample (0.0575 A/cm²) and pure epoxy coated (0.0306 A/cm²). Furthermore, the E_{corr} value for the mild steel sample shifted from -0.167V to 0.0368V. It was discovered that I_{corr} value shows a decrement with increase in rGO percentage and corresponding E_{corr} value increases. When compared to bare sample as well as pure EP coated specimen, composite coating containing rGO content of 1.0 wt.% had minimum I_{corr} rate (1.59×10^{-6} A/cm²) and the higher positive value of displacement for E_{corr} as 0.0759. Values of E_{corr} generally indicates the vulnerability to corrosion and the positive movement of I_{corr} specifies the barrier capacity of rGO and thereby considerably reduce the corrosion tendency of the covered mild substrate.

Apart from this the rate of corrosion of bare coated sample was 6.86 mil/yr., which was greater than rGO coated samples. In contrast composite coating with 1wt.% rGO content showed the least corrosion rate (0.351×10^{-3} mil/year) among all other percentages. The decrement in values can be assured due to the better dispersion of rGO nanoparticles and the impermeability property, that will suppress the penetration of corrosive chemicals. The chemical inertness of rGO deposited over the mild steel surface can be attributed to the corrosion resistance increase of the mild steel sample.

Furthermore, the R_p values of rGO coated samples are higher than pure epoxy coatings, which is consistent with E_{corr} and I_{corr} results are shown in Figure 5. The highest R_p value (23.7×10^6) Ω cm² was for the coating containing 1% rGO indicating the depletion capability of the steel substrate and the rise in R_p values clearly disclosed the protection against metal dissolution. In addition, the rGO/EP coating. Table 1 also figure out the values of β_a including highest values was indicated by rGO contained samples (1 wt.% rGO) signifying delay in the anodic reaction. It was observed that efficiency of rGO coated electrodes increased to 53.2%, along with this 1% rGO/EP coated mild steel electrode have greater inhibition efficiency (99.98%) was unquestionably greater than pure epoxy resin coated sample (46.78%).

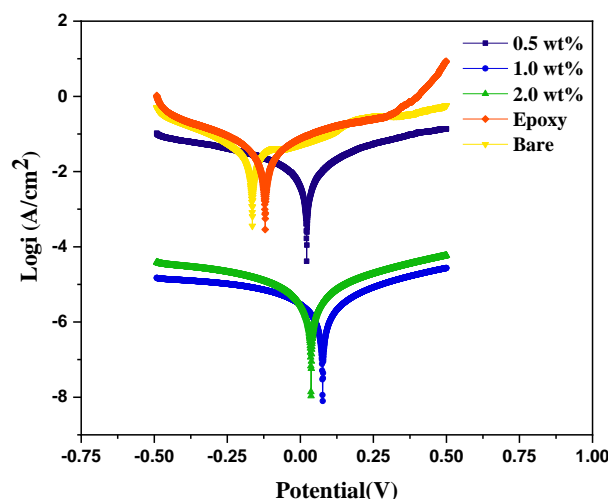


Figure 4. Polarization curves of mild steel coated with EP and different percentages of rGO/ Epoxy - composite coating after 24 hours of immersion in SCP containing 0.5M NaCl.

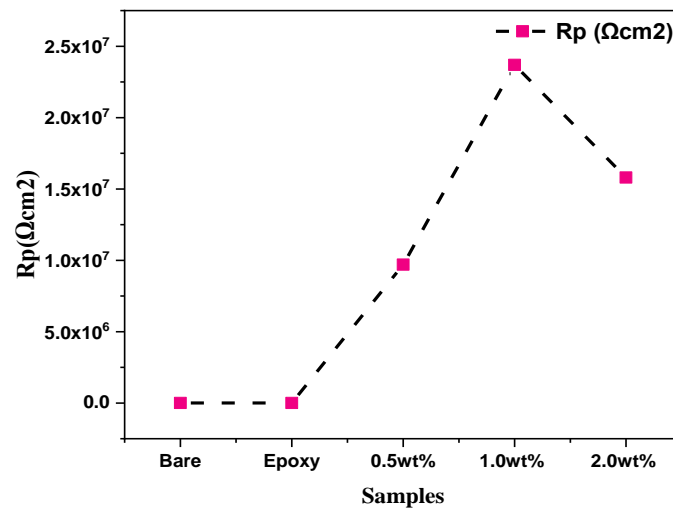


Figure 5. Polarization resistance of various coatings immersed in CPS containing 0.5M NaCl solution for a period of 24 hours.

Table 1. Corrosion parameters obtained from Tafel extrapolation for pure epoxy and rGO /EP coated samples after 24 hours immersion in CPS containing 0.5M NaCl solution.

Sample	E_{corr} (V)	I_{corr} (A/cm ²)	β_a (V/dec)	β_c (V/dec)	CR) (mil/year)	Efficiency ($\eta\%$)	R_p (Ωcm)
Bare	-0.167	0.0575	-4.97	6.327	6.86	-	1444
Epoxy	-0.1159	0.0306	-4.009	3.76	1.837	46.78	5484
0.5wt% rGO/EP	0.0288	6.516×10^{-3}	-7.15	6.4	7.214×10^{-3}	88.66	9.7×10^6
1.0wt% rGO/EP	0.0759	1.59×10^{-6}	-5.709	5.704	0.351×10^{-3}	99.98	23.7×10^6
2.0wt% rGO/EP	0.0368	5.019×10^{-5}	-7.098	6.013	2.43×10^{-3}	99.87	15.8×10^6

4. Conclusion

In this study the influence of rGO incorporated epoxy coating on anticorrosion behaviour of mild steel in simulated concrete pore solution containing NaCl medium was experimented systemically. Composite coating containing three different percentages of rGO particles compared with pure epoxy and bare samples. Coating comprising rGO showed greater corrosion resistant improvements when compared to pure epoxy coating. The OCP and EIS results demonstrated the enhancements in corrosion protection and excellent barrier properties of rGO. Due to its high impermeability, the addition of rGO nanoparticles to the coatings boosted its anticorrosion capacity. Results revealed that epoxy coating containing 1.0 wt.% rGO showed better corrosion resistant behaviour in concrete pore solution medium.

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