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Inhibition and promotion of electrochemical reactions by graphene in organic coatings

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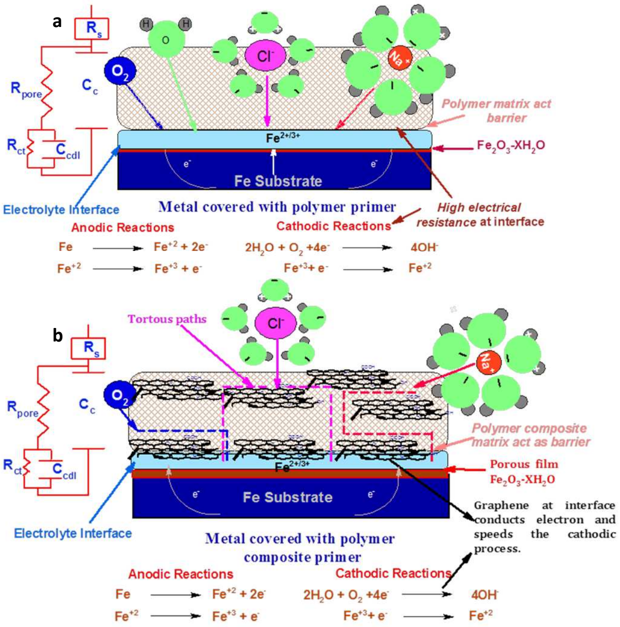
Time-dependent electrochemical properties of graphene nanoplatelets (GP) and self-crosslinked polyvinyl butyral (PVB) composites are dicussed. Electrochemical experiments in chloride medium revealed that GP offers short-term excellent protection from the physico-chemical mechanisms operating within the barrier. For longer periods of time, corrosion promotion was discovered due to induced porosity and electrochemical mechanisms related to excellent electrical conductivity and higher position in the galvanic series. This research has helped to understand the misleading anti-corrosion properties associated with graphene-polymer composites coatings.

The environmental constraints on using chromium (VI) based coatings has led towards the development of non-toxic organic and inorganic anticorrosion pigments incorporated in polymer coatings[1, 2]. Graphene sheets are one-atom-thick two-dimensional layers of sp^2-bonded carbon having a variety of remarkable properties and can enhance properties of polymers such as electrical and thermal conductivity, gas impermeability and mechanical properties, etc[3, 4].

Significant research has been conducted on the anti-corrosion properties of graphene in organic coatings which were due to its barrier nature towards corrosion promoting species. Recently, Yu *et al*. discussed about the anti-corrosion properties of modified graphene incorporated in polystyrene. The improved anti-corrosion properties of nano-composites were due to the impartation of barrier property in polystyrene[5]. Mayavan *et al*. also described the same phenomenon with composites of poly(sodium styrene sulfonate) and graphene[6]. Similar mechanisms were explained and can be found in the literature such as graphene/epoxy[7-9], polyimide/graphene[10], polyurethane/graphene[11] composites for anti-corrosion coatings. In the same manner, many studies have shown the single time barrier properties of stand-alone graphene films on the surface of aluminium, where excellent protection was shown after 0.5 hour of immersion in chloride environment[12]. Likewise, Raman *et al*. measured the anti-corrosion properties of graphene film on copper after 1 h of immersion.[13]

However, to date, anti-corrosion properties of graphene based polymer coatings were measured for a single point in time, which could mislead the long term protection. In this study, we measured time-dependent anti-corrosion properties of GP based PVB composite coating on carbon steel in 0.1M NaCl aqueous solution. Carbon steel samples were coated with thin film of self crosslinked composites of PVB and GP. We used the electrochemical techniques and measured the corrosion properties after immersion time of 1 and 26 h to differentiate between the corrosion barrier and corrosion promoting phenomena associated with graphene based composites coatings.



Scheme 1 Corrosion protection phenomena in the absence a) and presence b) of GP in PVB (cross-sectional view) with electrochemical corrosion models for 26 h immersion in 0.1 NaCl

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Electronic Supplementary Information (ESI) available: Experimental Procedure, OCP of Coatings, FE-SEM of composite coating morphology, TEM, FTIR, TGA, Raman, bulk conductivity of GP and XRD of GP and Graphite, TGA, DSC, FTIR of PVB, FTIR of PVB/GP composites, Camera image and XPS of corroded surface. DOI: 10.1039/x0xx00000x

Table 1 Electrochemical parameters obtained from OCP, EIS and PD for different samples [a]1.5% probable Error, [b]9% probable error , [c]8% probable error, [d]10% probable error, [f]5% probable error, [i]20% probable error

T (h)	S. No.	[a]ocp mV	[b]R_{pore} $\Omega.cm^2$ $\times10^3$	[c]C_C $F.cm^2$ $\times10^{-04}$	[d]R_{ct} $\Omega.cm^2$ $\times10^3$	[e]C_{dl} $F.cm^2$ $\times10^{-4}$	[f]E_{corr} mV	[i]i_{corre} A/cm^2 $\times10^{-6}$
1	**PVB**	-525	1.17	4.47				
	G-1	-450	2.22	4.11	-	-	-	-
	G-2	-460	3.98	4.34	-	-	-	-
26	**PVB**	-617	0.68	4.84	1.05	1.07	-663	4.6
	G-1	-607	0.62	6.24	0.82	2.56	-584	8.0
	G-2	-627	0.65	9.36	1.04	3.63	-615	9.7

Scheme 1 describes general physicochemical and electrochemical mechanisms of corrosion protection and promotion respectively due to the incorporation of GP in organic coatings[14]. The short term protection is explained by physicochemical mechanism which is generally associated with the obstruction of corrosive agents. This effect may be enhanced significantly by incorporating plate like reinforcements, thus, increasing the diffusion length for the corrosion agents to reach at the defects through microscopic pores. For reinforcement-free organic coating coatings, the basic mechanism is separation of metal surface from the environment. The permeability of organic coatings also depends on the nature of the binder matrix. In this study, we used crosslinked film (Figure S-7b ESI†) of PVB coating in order to have enhanced barrier nature of binder. The long term corrosion promotion effect was explained by the 'active' nature of GP in the coatings. As water molecules start to accumulate at the interface, which facilitates the corrosion under the coating, graphene nanoplatelets stimulate the electrochemical reaction due to the conductivity of electrons at the interface[15]. This effect was also explained by addition of carbon black to the zinc filled coating where carbon black was observed to promote the corrosion and acted as perfect cathode for zinc. The addition of carbon black also improved electrical connections between the zinc particles promoting the galvanic effect[16]. In addition, it was also reported that incorporating carbon increased the porosity of the organic coating and increased the absorbance of water, thus, promoting the corrosion[17]. It was also reported that 1 g of reduced graphene (rG) sorbed 14 g of water[18]. In order to study the line of defence for each mechanism, we used thin coating i.e. 70 ±5 µm (Figure S-6 ESI†) having very low solid contents[6] of binder (0.2 wt/v %) and GP (0.1 and 0.2 wt/v %). PVB and GP were used in two different ratios i.e. PVB:GP were 2:1 and 1:1.

EIS is a powerful tool for explicating the behaviour of coating resistance and water absorption[19]. Here we utilized EIS to examine the characteristics of defects arising in PVB and PVB/GP composites coatings presented by complex plane plots. The coating shows porous structure and non-ideal capacitive behaviour (see Figure 1 and Table 1). The pore resistance of coating reduced with the addition of GP which indicates the increased ionic resistance to current flow between the bulk and interface[20]. At the initial stage of immersion (1 h), G-2 coating exhibit quasi-ideal resistive behaviour. The pore resistance of G-2 was observed to be very high as showed by half semicircle of Nyquist plot indicating the strict barrier nature of coating, resulting in the hindrance of faradic reactions. As shown by Scheme 1, this barrier nature could be explained by the low diffusivity of corrosion reactants due to GP sheet like structure (Figure S-9 ESI†) [21]. The pore resistance of coatings was calculated by following equation[13]

$$|Z| = \sqrt{Z_{real}^2 + Z_{imaginary}^2}$$

At lowest frequency, where $Z_{imaginary} \rightarrow 0$ giving $|Z| = Z_{real}$ in Bode plot. It is also evident from Bode plots of Figure 1a that the pore resistance of G-1 and G-2 was at least 50% and 70% respectively greater than that of PVB coated steel after 1 h of immersion. With increasing exposure time i.e. 26 h of immersion, it was taken in to account that corrosive media had accumulated at the carbon steel surface through the coating. EIS data from Figure 2a and Table 1 shows the variations in the impedance model as response to intact area. The change in the EIS plots indicated that the model used for 1 h of immersion did not satisfy for longer period immersion. It can be noticed that coating capacitance of G-1 and G-2 was increased by 23% and 50% respectively. Similarly, interface capacitance of G-1 and G-2 had increment of 58% and 71% respectively showing enhancement of corrosion. Although, there was not much difference in the coating and charge transfer resistance, but these parameters showed decreased value for G-1 and G-2. The presence of water in the pores can change the dielectric constant of the coating or interface and it can be determined by the capacitance[20]. The increased capacitance values with increased exposure time for G-1 and G-2 indicated that presence of corrosive reactant and products in coatings and coating/metal interface changed the local effective dielectric constant and water uptake properties according to following equations[21, 22].

$$C = \frac{\varepsilon\varepsilon_0 r}{d} \text{ and } \theta(\%) = \frac{\log(C_t/C_o)}{\log(\varepsilon_w)}$$

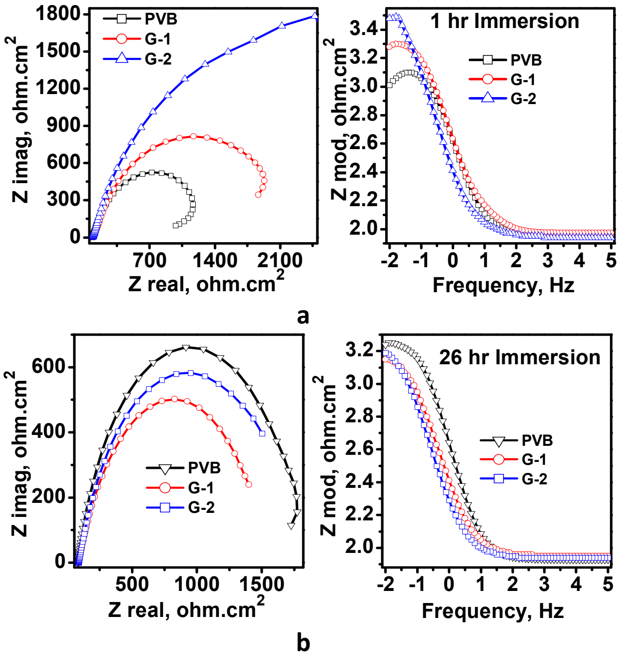
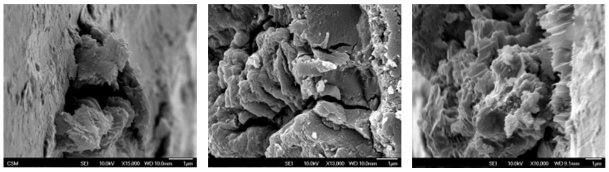


Fig.1 EIS magnitude spectra of coated carbon steel after a) 1 h and b) 26 h immersion in 0.1 M NaCl



PVB, 1.82% G-1, 9.5% G-2, 17.5%

Fig.2 Cross-sectional area of coating showing coating/metal interface and water uptake θ(%) after immersion of 26 h

where d is layer thickness, ε is relative dielectric constant, ε_o is permittivity of free space, r is layer surface and C is capacitance, θ is percentage of water uptake C_t is the coating capacitance at 26h, C_o is initial coating capacitance at 1 h, and ε_w is the relatively permittivity of water taken as 80.1 at 20 °C. It can seen from Figure 2 that addition of GP enhanced the water uptake percentage to 9.5% for PVB to GP ratio of 2:1 and almost double with the 1:1 ratio of PVB to GP. These results have conformity with the previous work reported on coatings containing carbon black[17]. SEM images were taken at cross-sectional area to study the morphological alterations of coatings at metal/coating interface. The corrosion effects can be confirmed in Figure 2 where larger defects could be observed for G-1 and G-2. The approximate defect size of coating for PVB and GP was around 5 µm and 10 µm respectively.

Figure 3 and Table 1 show the anodic and cathodic polarization curves and corrosion kinetics parameters i.e. i_{corr} and E_{corr} for PVB and GP/PVB coated carbon steel obtained after immersion of 26 h in 0.1M NaCl. The i_{corr} (current density) represents the rate at which reduction and oxidation reactions become equal at E_{corr}(Corrosion potential). The i_{corr} value of PVB coated steel was nearly 50% lesser than G-1 or G-2 suggesting that the incorporated GP in PVB coating remarkably accelerated the corrosion processes at the interface after the destruction of barrier properties. The long term reduction in protection behaviour of GP/PVB can be attributed to the presence GP in coating which acted as cathodic to the iron at interface and increased the anodic process[15]. The electrical conductivity (see ESI†) of GP had also strong influence on the enhancement of corrosion process. The protection offered by organic coating is owing to the high electrical resistance above the interface thus preventing external flow between anodic and cathodic areas. It is believed that if the electrical resistance of the coating is maintained at a very high level, the electrochemical corrosion cannot occur. The presence of GP in coatings enhanced the electrical contact across the iron surface and maintained the charge transfer for the electrochemical reactions below the coating[15] as shown in Scheme 1. The increased current density shows the enhanced flux of electrons throughout the electrochemical system in equilibrium. These findings were also supported by the optical micrographs of coated carbon steel (Figure 3). All of the samples were found to be corroded. Figure 3 also revealed that corrosion underneath the coating is more for G-2 and G-1 than PVB.

Figure S-3 (a-b) ESI† shows variations in open circuit potential over a period of 1 and 26 h. Both G-1 and G-2 found to be 80 mV noble after 1 h due to the barrier properties of the coatings. During 1 hour of the immersion, all of the coatings have rapid and continuous decreasing trend toward negative direction indicating the adsorptions of corrosive media in the coatings. During 26 h of immersion, OCP curves for all coatings, clearly demonstrating the pronounced effect of charge transfer reactions and uniform corrosion for first and second half of the curves respectively[23]. These results are in accordance with the EIS and PD.

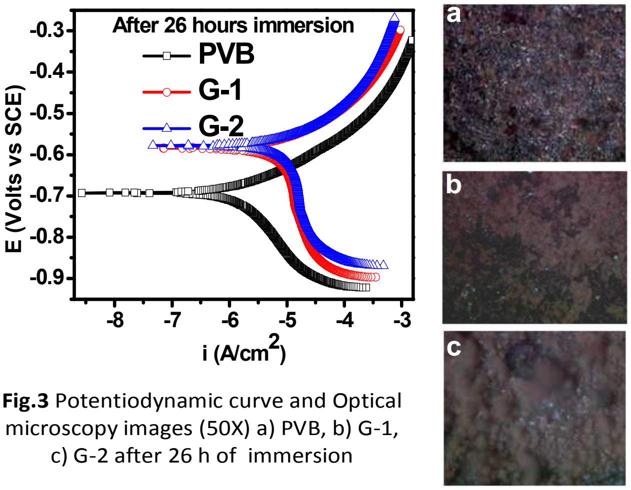


Fig.3 Potentiodynamic curve and Optical microscopy images (50X) a) PVB, b) G-1, c) G-2 after 26 h of immersion

XPS spectra for O1s (See Figure S-15 ESI†) show mixers of iron oxide compounds on the corroded surface. The corrosion products mainly contained different forms of iron oxide including Goethite (αFeOOH), Wüstite (FeO), hydrated iron oxide ($Fe(OH)_3$) and Hematite (αFe_2O_3)[24] for all the cases. It can be concluded that presence of graphene does not affect the formation of corrosion products.

Conclusions

Electrochemical techniques such as OCP, EIS and PD were used to explain anti-corrosion properties associated with barrier behaviour and corrosion promoting properties associated with electrochemical reaction in organic coatings. Graphene shows excellent short-term anti-corrosion properties, but for longer periods of time, this effect becomes worse and corrosion promotion effect is observed.

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