

## ***Effect of Incorporating TiO<sub>2</sub> on the Corrosion Inhibition Behaviour of Poly(butadiene-co-acrylonitrile)-Polyaniline Dodecylbenzenesulphonate (NBR-PAni.DBSA) Blends***

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*A pre-optimised poly(butadiene-co-acrylonitrile)-polyaniline dodecylbenzenesulphonate (NBR-PAni.DBSA) blend with useful electrical conductivity (in the region of  $10^{-3} \text{ S.cm}^{-1}$ ) was prepared and the effect of incorporation of titanium oxide (TiO<sub>2</sub>) on its corrosion inhibition behaviour for carbon steel was successfully assessed for the first time. It was found that the electrical conductivity of this blend can be enhanced up to a magnitude order for TiO<sub>2</sub> loadings, 20.0-22.5 wt %. As found from both total immersion and electrochemical corrosion tests, NBR-PAni.DBSA blends with 20.0-22.5 wt % of TiO<sub>2</sub> are deemed to be the best corrosion inhibitor for carbon steel, either in acid or artificial brine environment. However, a blend consisting of very high TiO<sub>2</sub> content (i.e. 25.0 wt %) showed a significant poorer corrosion inhibition behaviour for carbon steel due to its more serious phase separation and porosity problem between the NBR host matrix and TiO<sub>2</sub>.*

**Keywords:** Corrosion inhibition; nitrile rubber; polyaniline; carbon steel; titanium dioxide

Intrinsically electrically conductive polymer (ICP), especially polyaniline (PAni) has received the most attention in the field of corrosion science due to its ease of preparation, excellent environmental stability and feature of redox properties associated with the nitrogen chain<sup>1-7</sup>. ICP based organic coating also has the capability of providing the ideal physical barrier coating against corrosion if compared to other organic coatings under the attack of some aggressive species, e.g. O<sub>2</sub> and H<sup>+</sup><sup>1-8</sup>. PAni was regularly doped with

either hydrochloric acid or sulphonic acid or phosphonic acid or dioctyl phosphate or camphor sulphonic acid when it was used in the corrosion inhibition coating<sup>1-7</sup>.

ICP based coating is mainly functioned as the primary coating for the corrosion inhibition of carbon steel, which is due to the formation of passivating stable oxide films, e.g. Fe<sub>3</sub>O<sub>4</sub>,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> at the metal-ICP interface<sup>9-10</sup>. These dense oxide layers are acting as the protecting physical barrier that

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may avoid the metal surface from further attack by all corrosive species<sup>9-10</sup>. There are a few reasons that limit the pure PANi's application in terms of corrosion inhibition, *i.e.* the brittleness and poor adhesion of pure PANi to its substrate, particularly in the corrosive environment<sup>3,11-13</sup>. In order to overcome all these shortages, one can prepare a composite based on elastomer and doped PANi<sup>1</sup>.

It is also proposed here that a combined corrosion protection technique can be utilised in order to further enhance the corrosion inhibition property of this type of blend. Hence, some mineral particles can be added into organic coatings in order to enhance their corrosion inhibition property. These mineral particles may protect the metal by a combination of physicochemical and electrochemical mechanisms<sup>14</sup>.

Yoneyama<sup>15-18</sup> tried to co-deposit some mineral oxides into an ICP based matrix by using inert electrodes made of indium tin oxide (ITO) or gold (Au) in an electrolytic system without any stirring. A very low concentration of TiO<sub>2</sub> composition was unfortunately achieved, which was only up to 1.15 wt %. Domenech<sup>19</sup> introduced TiO<sub>2</sub> into an ICP matrix during electrochemical synthesis on carbon steel under magnetic stirring and successfully produced composite films with up to 6.5 wt % TiO<sub>2</sub> concentration. These composites showed a slight improvement in term of the corrosion protection for carbon steel. Beck<sup>20</sup> demonstrated that strong convection is an important factor for incorporating TiO<sub>2</sub> into an ICP matrix. A concentration up to 17.0 wt % was achieved by using platinum or stainless steel as working electrodes in a 0.1 M LiClO<sub>4</sub> aqueous medium. Lenz<sup>8</sup> prepared an ICP-TiO<sub>2</sub> composite via the method of electrochemical synthesis in order to study its anti-corrosion property on carbon steel. High TiO<sub>2</sub> incorporation (about 18.0 wt %) was

obtained only with the presence of a chemical surfactant.

This work aims to study an pre-optimised electrically conductive rubber formula based on poly(butadiene-co-acrylonitrile) (NBR) and dodecylbenzenesulphonate acid doped PANi (PANi.DBSA) with various loadings of TiO<sub>2</sub> for the corrosion inhibition enhancement of carbon steel. These blends were solution mixed in a solvent, *i.e.* toluene. NBR has been focused here due to its excellent chemical, oil, heat ageing, abrasion, water and gas permeability resistances. Meanwhile, PANi.DBSA was selected here due to its low toxicity, good thermal stability, high electrical conductivity, good compatibility with NBR and well established synthesis method<sup>21-27</sup>.

Electrical conductivities of these TiO<sub>2</sub> loaded NBR-PANi.DBSA blends were determined. Morphological study using transmission electron microscopy (TEM) was performed in order to assess the compatibility level of all these constituent components. Two techniques were also carried out to study the corrosion inhibition behaviour of these blends, *i.e.* (a) a total immersion corrosion test in 5 wt % sodium chloride aqueous solution and (b) an electrochemical test with a potentiostat system.

## EXPERIMENTAL

### Chemicals and Raw Materials

Aniline monomer (99 wt %, Sigma-Aldrich), ammonium persulphate (APS) (98 wt %, Sigma-Aldrich), 36.5-38 wt % hydrochloric acid (HCl) solution (GPR), ferric chloride (FeCl<sub>3</sub>) solution (purum, 45% FeCl<sub>3</sub> basis, Sigma-Aldrich), 33 wt % ammonia solution (GPR, Sigma-Aldrich), 70 wt % dodecylbenzene sulphonic acid (DBSA) solution in 2-propanol (GPR, Sigma-

Aldrich) and methanol (GPR) were used for the synthesis of PANi.DBSA. Commercial grade NBR (Krynac<sup>®</sup> 50.75, manufactured by Bayer Germany) was selected as the elastomeric host. The NBR was washed with methanol for 24 h using soxhlet extraction in order to remove chemical additives. By <sup>1</sup>H-NMR analysis of solutions in THF-d<sub>8</sub>, the actual acetonitrile (ACN) content for NBR was determined as 48.2±1.0 wt %. Pure PANi.DBSA, NBR Krynac<sup>®</sup> 50.75 and toluene have solubility parameter values of 20.8, 20.7 and 18.3 (MJ m<sup>-3</sup>)<sup>0.5</sup>, respectively<sup>21</sup>. Both NBR and PANi.DBSA were highly soluble in toluene (GPR, Sigma-Aldrich). High dispersible TiO<sub>2</sub> in the form of nano-powder (with purity about 99.7%) was supplied by Sigma-Aldrich. It is not soluble in organic solvent and has an average particle size <25 nm.

### Synthesis of PANi.DBSA

Conductive emeraldine salt PANi.HCl was synthesised by the oxidative chemical polymerisation technique based on an oxidant (APS)/monomer (aniline) initial molar ratio of 1.0. 50 mL of aniline and 125.2 g of APS were dissolved in 375 mL and 276 mL of 2 M HCl respectively, which had been pre-cooled to 1°C. The aniline solution was placed in an ice bath with an overhead stirrer. After the addition of FeCl<sub>3</sub> solution (about 1 mL) as a catalyst, the APS solution was added gradually over a period of 20 min, with constant stirring to ensure thorough mixing. The temperature of the polymerisation mixture was maintained to ≤2°C while the pH was adjusted to be ≤1.0 by the addition of concentrated HCl. The mixture was left for 6 h to complete the polymerisation, and the precipitate was allowed to settle before decanting and final washing with distilled water until the filtrate was colourless. PANi emeraldine base (EB) was prepared by de-protonating the wet PANi.HCl in 33% aqueous ammonia solution (about 5000 mL)

with 24 h stirring, followed by washing and re-protonation in 1M aqueous DBSA at a molar ratio EB:DBSA of 1:1. Filtration was performed with a sintered-glass funnel of grade 3 porosity (16–40 microns). All products were washed with large quantities of distilled water until the filtrates were colourless and no odour of ammonia could be detected. Final drying of the powdered filter cake was done in a vacuum oven at 50°C for 24 hours. A sample of PANi.DBSA synthesised here was submitted for elemental analysis at the Malaysian Rubber Board Characterisation Laboratory, and was estimated thereby to have a 42% protonation level on the basis of the S:N atomic ratio.

### Blend Preparation

Masterbatch solutions of pure NBR (50 mg NBR/mL solvent) and PANi.DBSA (16.5 mg PANi.DBSA/mL solvent) in toluene were first prepared and filtered. The pure NBR solution was then added to the PANi.DBSA solution in appropriate amounts in order to obtain a pre-optimised composition, *i.e.* 70.0 wt % NBR: 30.0 wt % PANi.DBSA<sup>1</sup>. Hydroquinone of 1.0 wt %<sup>27–28</sup> was added to the blend solution as the compatibiliser. This hydroquinone added blend solution were divided into eight portions. After that, 2.5, 5.0, 7.5, 10.0, 12.5, 15.0, 17.5, 20.0, 22.5 and 25.0 wt % of TiO<sub>2</sub> were respectively added to each of the blend solution. A control sample without any addition of TiO<sub>2</sub> was also prepared. Finally, each of these blend solutions was magnetically stirred for 48 hr at 50°C prior to casting/coating.

### Determination of Electrical Conductivity

The DC electrical conductivities for PANi.DBSA, pure NBR and their blends (with and without TiO<sub>2</sub>) were calculated from electrical resistances measured by guarded 2-probe technique. The equipment employed was a

Keithley 6517A Electrometer (with built in-voltage source up to 1kV). Pressed pellets of pure PAni.DBSA and TiO<sub>2</sub> (diameter 13 mm, thickness 1.5 mm) were prepared respectively. Each pellet was placed in a holder with two spring-loaded metallic contacts in order to measure its electrical resistance. Samples of pure NBR and blend were cast respectively from their solution onto square microscope slides (625 mm<sup>2</sup>), and the solvent was allowed to evaporate for 24 h in a vacuum oven at about 100°C.

Electrical conductivities were calculated from the mean resistance values (based on a set of five samples) obtained by the 2-probe method using Equation 1<sup>21</sup>.

$$\sigma = \left(\frac{1}{R}\right) \left(\frac{L}{A}\right) \quad \dots 1$$

where  $\sigma$  is the electrical conductivity,  $R$  is the mean value of apparent resistance (voltage/current) for the cast blend,  $L$  is the measured electrode spacing distance and  $A$  is the cross-sectional area of the electrode, which is in close contact to the cast film.

### Morphological Study (Transmission Electron Microscope)

All NBR-PAni.DBSA blends (with and without TiO<sub>2</sub>) were studied by using a transmission electron microscope (Philips CM12 microscope, at accelerating voltage 80 kV). Ultra-thin (ca. 150 nm) samples of each blend (frozen with liquid nitrogen) were obtained for this study by sectioning with a microtome.

### Total Immersion Corrosion Test

The immersion test technique is the most common corrosion test used for carbon steel

samples, coated with synthesised pigments. All prepared blend solutions were kept in an air tight jar to avoid any solvent evaporation. Carbon steel samples of circular shape were cut from sheet (not bar stock) in order to minimise the exposed end grain according to the *ASTM G31* standard<sup>29</sup>. The samples were polished by fine size emery paper (600 grit), cleaned, degreased with acetone (GPR, Sigma-Aldrich), dried and weighed with an electronic balance (Mettler Toledo AL204, accuracy of  $\pm 0.1$  mg). Sample shape and size were made convenient to laboratory corrosion tests according to the *ASTM G31* standard<sup>29</sup>. Three sets of test samples with respective diameter of about 38 mm and thickness of approximately 3 mm, with a hole of about 8 mm in diameter were prepared for each blend. First, each test sample was dip-coated for 1 min in the related blend solution and then left for 1 hr to dry; the second dip was for another 1 min then dried in an oven for 48 h at 40°C.

After the end of immersion test period (60 days) in 5.0 wt % sodium chloride aqueous solution, the test samples were taken out and the coating removed and cleaned according to *ASTM G1* standard<sup>29</sup>. The performance of the coating was assessed through calculation of the mean value of sample's mass loss.

### Electrochemical Corrosion Test

Each NBR-PAni.DBSA blend (with or without TiO<sub>2</sub>) coated carbon steel sample was mounted to the working electrode (at the bottom of the rod that was directly exposed to the electrolyte). Epoxy resin (Dow<sup>TM</sup>, D.E.R. 671-T75) was used to seal up all edges. The electrochemical corrosion test was performed by using a system based on the Wenking M Lab potentiostat (Bank Elektronik-Intelligent Control GmbH, Germany) in a standard corrosion test cell equipped with a platinum-counter electrode and a saturated calomel

reference electrode (SCE). The scanning rate was tuned to  $2.0 \text{ mVs}^{-1}$ . All potential values here are reported in terms of reference to the SCE. All measurements were done at room temperature ( $\sim 23^\circ\text{C}$ ) and the chosen electrolyte was either HCl (0.1 M) or 5.0 wt % sodium chloride aqueous solution.

## RESULTS AND DISCUSSION

### Determination of Electrical Conductivity

Pure NBR is a good electrical insulator, with conductivity in the region of  $10^{-14} \text{ S.cm}^{-1}$  and the in-house synthesised PANi.DBSA showed a high electrical conductivity of  $1.5 \pm 0.5 \text{ S.cm}^{-1}$ . Meanwhile, the  $\text{TiO}_2$  used here recorded an intermediate electrical conductivity in the region of  $10^{-6} \text{ S.cm}^{-1}$ . The calculated mean electrical conductivity values for all pre-optimised NBR-PAni.DBSA blends (with and without  $\text{TiO}_2$ ) are shown in *Figure 1*.

Electrical conductivities of all blends are generally enhanced with the loading of  $\text{TiO}_2$ . Blends prepared with 20.0-22.5 wt % of  $\text{TiO}_2$  contents showed highest electrical conductivity values in the region of  $10^{-2} \text{ S.cm}^{-1}$ , which were about a magnitude order higher than the one without addition of  $\text{TiO}_2$ . It is proposed that the addition of this semiconductive  $\text{TiO}_2$  does not affect those electrical conductive pathways built up by PANi.DBSA particles<sup>21-27</sup>. At the same time, it is also envisaged that these highly dispersible semiconductive  $\text{TiO}_2$  particles also help to strengthen up the electrical conductive network within the NBR host matrix (*Figure 2*).

### Morphological Study

All NBR-PAni.DBSA blends (with and without  $\text{TiO}_2$ ) were studied by using a transmission electron microscope and

all obtained micrographs were showing similar morphological features. Hence, only micrographs of blends with 5.0, 20.0 and 25.0 wt % PANi.DBSA are shown in *Figure 2* as the example. For these blends, all dark coloured regions are phase separated, large and elongated conductive PANi.DBSA particles and their agglomerates. Meanwhile, all light coloured regions are related to well-blended NBR and  $\text{TiO}_2$ . However, those light coloured regions are getting denser in colour while increasing the content of  $\text{TiO}_2$  (*Figures 2a-2c*). Just like the PANi.DBSA, these very fine  $\text{TiO}_2$  particles (with average size  $<25 \text{ nm}$ ) will also encounter phase separation when they are getting saturated in the NBR host matrix. As reported by Lenz<sup>8</sup>, an ICP based composite with high  $\text{TiO}_2$  concentration (about 18.0 wt %) could lead to an increase of porosity and phase separation. The same occurrence is being observed for blends with 25.0 wt % of  $\text{TiO}_2$  (*Figure 2c*) in this work. This is why the electrical conductivity value of this particular blend dropped back to the original region of  $10^{-3} \text{ S.cm}^{-1}$  (*Figure 1*).

### Total Immersion Corrosion Tests

*Figure 3(a)* shows all mean values of total mass loss from carbon steel samples at the end of immersion test period, *i.e.* 60 days. *Figure 4* shows the influence of the aggressive media on the samples at the end of the test period. The efficiency of pre-optimised NBR-PAni.DBSA coatings (in different contents of  $\text{TiO}_2$ ) against corrosion can be directly assessed from this test. As can be seen, the control sample (coated with pre-optimised NBR-PAni.DBSA blend) recorded the highest mass loss in this study (*i.e.* 1.47% of the original sample's weight before the test). Meanwhile, samples coated with high  $\text{TiO}_2$  contents (*i.e.* 17.5-22.5 wt %) showed the least degradation and rust development. The greatest inhibition in the rust development was found for the



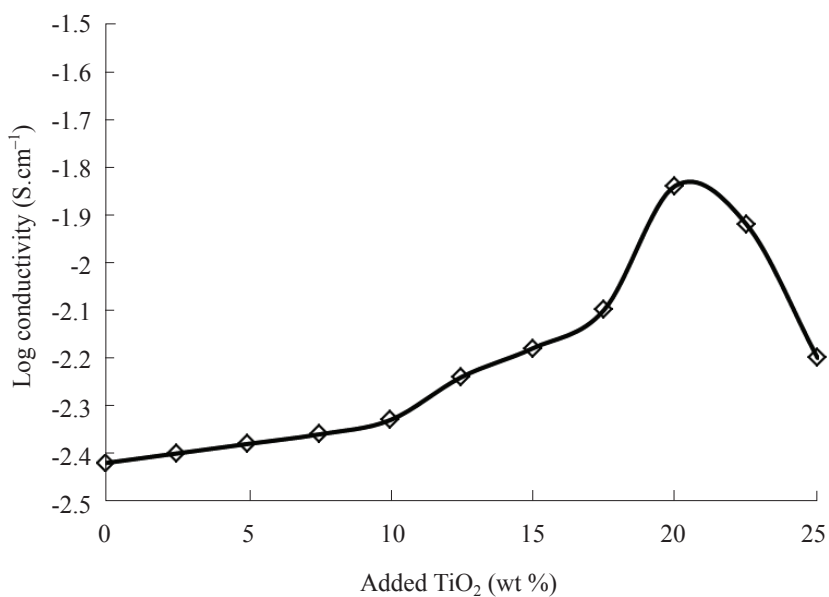


Figure 1. Electrical conductivities for pre-optimised NBR-PAni.DBSA blends (70.0 wt % NBR: 30.0 wt % PAni.DBSA) as a function of TiO<sub>2</sub> loading (wt %).

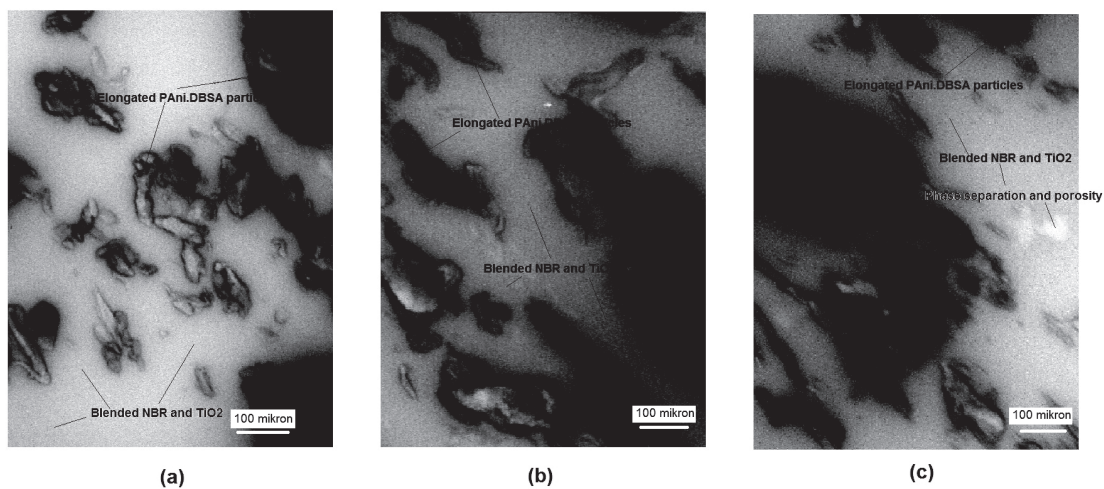


Figure 2. Transmission electron micrographs of pre-optimised NBR-PAni.DBSA blend (70.0 wt % NBR: 30.0 wt % PAni.DBSA). (a) Blend with 5.0 wt % of TiO<sub>2</sub>, (b) Blend with 20.0 wt % of TiO<sub>2</sub> and (c) Blend with 25.0 wt % of TiO<sub>2</sub>.

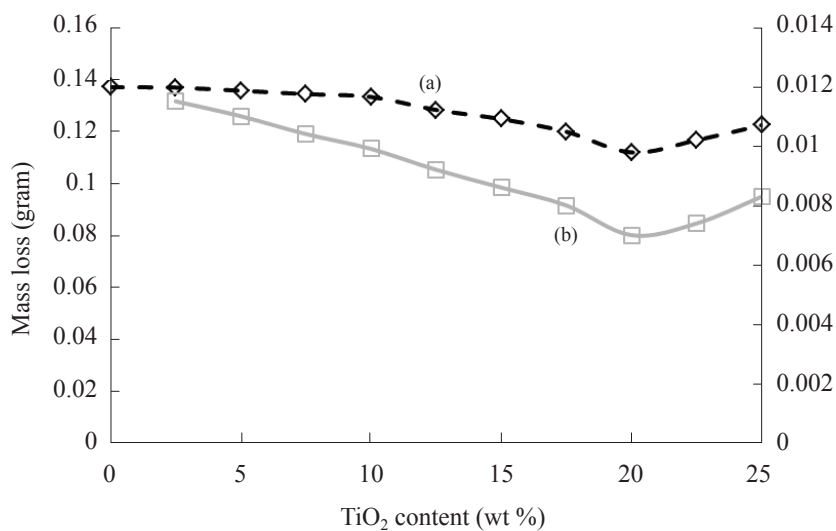


Figure 3. (a) Mean values for total mass loss for carbon steel samples versus their  $\text{TiO}_2$  coating contents (wt %) and (b)  $i_{corr}$  values of carbon steel samples versus their  $\text{TiO}_2$  coating contents (wt %).

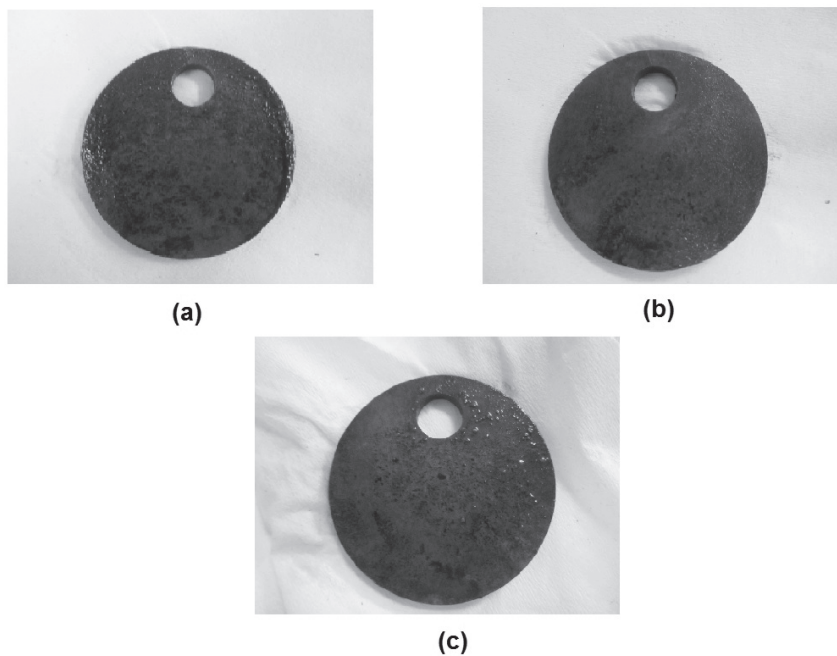


Figure 4. Carbon steel samples after 60 days fully immersion corrosion test in 5.0 wt % sodium chloride aqueous solution. (a) Control sample; (b) Sample coated with 20.0 wt %  $\text{TiO}_2$ ; (c) Sample coated with 25.0 wt %  $\text{TiO}_2$ .

sample coated with 20.0 wt % of TiO<sub>2</sub>. This particular sample also revealed the lowest mass loss, *i.e.* 1.20% of the original sample's weight. However, for samples coated with 25.0 wt % TiO<sub>2</sub>, a more serious corrosion had occurred and this was due to the increased phase separation and porosity between NBR host matrix and TiO<sub>2</sub> (Figure 2c).

### Electrochemical Corrosion Tests

Figure 5 shows some examples of corrosion potential against time for samples coated with pre-optimised NBR-PAni.DBSA blends (*i.e.* with TiO<sub>2</sub> contents, 0.0, 20.0 and 25.0 wt %) in 0.1 M HCl solution. In this figure, -0.165 V represents the corrosion potential of pure carbon steel. The sample coated with 20.0 wt % TiO<sub>2</sub> content had the most positive potential

value among all tested samples. In other words, the NBR-PAni.DBSA blend with 20.0 wt % TiO<sub>2</sub> content exhibited the best corrosion inhibiting behaviour in the acid environment. Besides this, corrosion potentials of all analysed samples stayed almost unchanged for over 60 minutes. Coatings with high TiO<sub>2</sub> contents, 25.0 wt % suffered a more serious phase separation and porosity problem (in consistent with the morphological result). H<sup>+</sup> and other ions could penetrate this coating easily through voids of the phase separated NBR and TiO<sub>2</sub>. For coatings with  $\leq 22.5$  wt % of TiO<sub>2</sub> content, most of these voids were covered due to the less phase separation between NBR and TiO<sub>2</sub>. The high content of NBR is strongly believed to be able to unite both PAni.DBSA and TiO<sub>2</sub> particles into a good network and subsequently enhance the corrosion inhibiting behaviour.

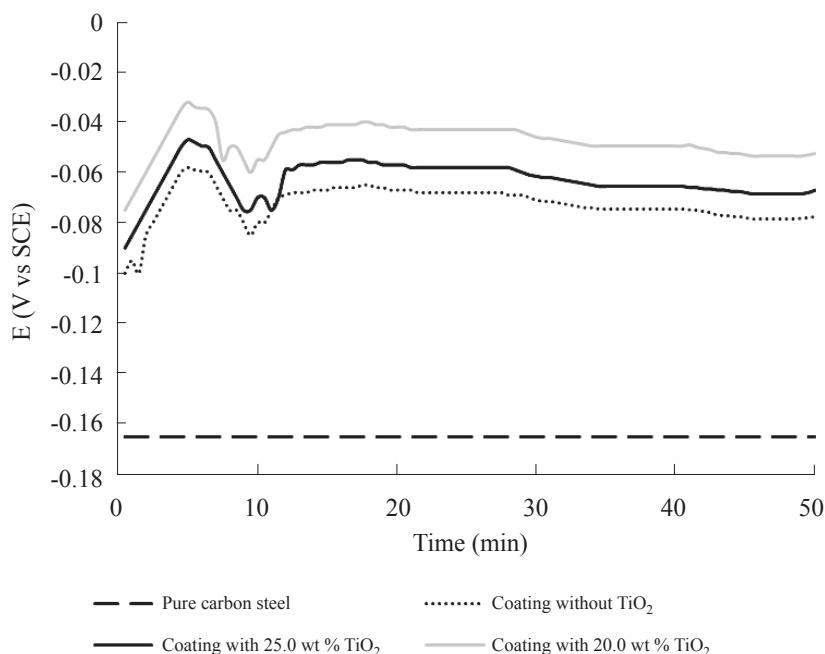


Figure 5. Plot of open circuit potential in 0.1 M HCl solution versus time.



Figure 6 shows some examples of corrosion potential against time for samples coated with pre-optimised NBR-PAni.DBSA blends (*i.e.* with  $\text{TiO}_2$  contents, 0.0, 20.0 and 25.0 wt %) in 5.0 wt % sodium chloride aqueous solution. The NBR-PAni.DBSA blend with 20.0 wt %  $\text{TiO}_2$  content again showed the best corrosion inhibiting behaviour in the sodium chloride solution. At the same time, a decreasing trend of corrosion potentials for all coated samples is also observed; which indicating the corrosion process was taking place slowly over a relative period. Both Figures 5 and 6 suggest that  $\text{H}^+$  is the main corrosion source for this kind of coating and through incorporation of  $\text{TiO}_2$ , the corrosion inhibiting behaviour could be further improved to a certain degree.

Tafel plots were obtained by scanning the potential from  $E_{\text{corr}}$  to -250 mV versus  $E_{\text{corr}}$  (cathodic plot) or to +250 mV versus  $E_{\text{corr}}$  (anodic plot). Figure 7 shows an example plot for sample coated with 20.0 wt %  $\text{TiO}_2$  in

the 5.0 wt % sodium chloride aqueous solution. The corrosion current ( $i_{\text{corr}}$ ) was determined by superimposing a straight line along the linear portion of the cathodic or anodic curve and extrapolating it to  $E_{\text{corr}}$ , as illustrated in Figure 7. Correspondingly, the slope of the straight line is the cathodic or anodic Tafel's constant ( $\beta_c$  or  $\beta_a$ , respectively). The corrosion current should be directly proportional to the corrosion rate. The determined  $i_{\text{corr}}$  values of all coated samples are summarised and presented in Figure 3b. As observed from Figure 3b, all coated samples could prohibit the absorption of water and ions quite efficiently. Coated samples with 20.0-22.5 wt % of  $\text{TiO}_2$  were less corroded even after 2 weeks in the laboratory environment upon completing the electrochemical measurement. Hence, it is strongly believed that a stronger corrosion inhibiting behaviour for carbon steel can be achieved through the incorporation of  $\text{TiO}_2$  into this type of blend due to the extra physicochemical

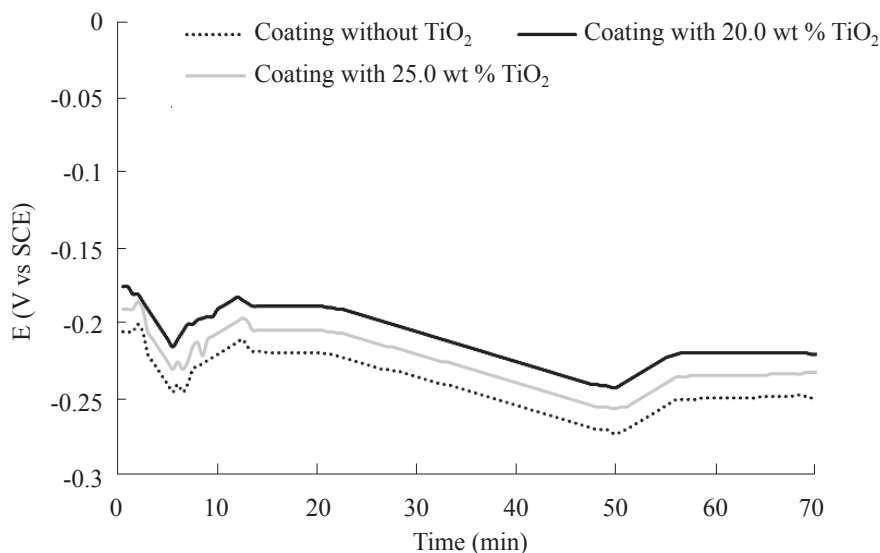


Figure 6. Plot of open circuit potential in 5.0 wt % sodium chloride aqueous solution versus time.

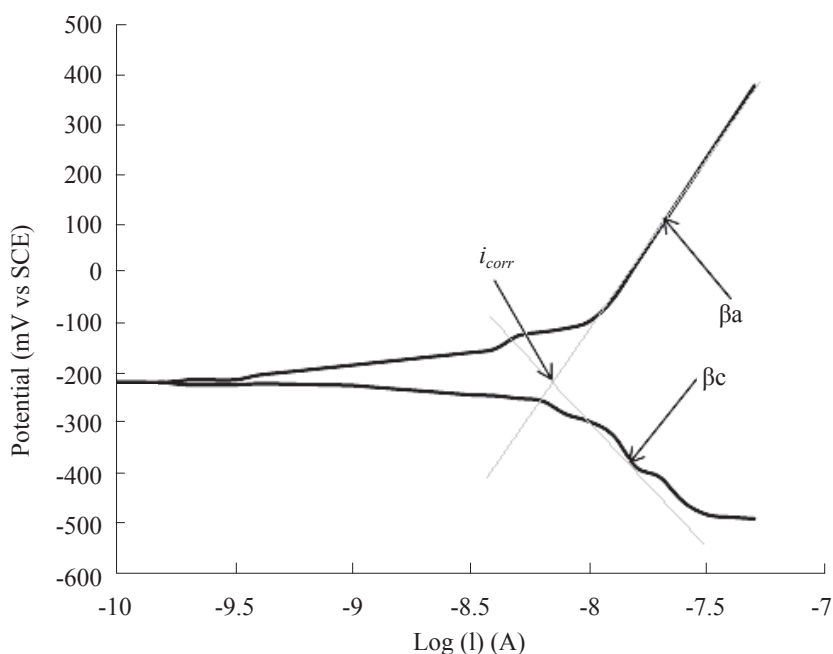


Figure 7. Tafel plot for sample coated with 20.0 wt % TiO<sub>2</sub> in 5.0 wt % sodium chloride aqueous.

protection<sup>14</sup>. All results obtained from the electrochemical test are in agreement with the immersion test.

### CONCLUSION

The effect of incorporating TiO<sub>2</sub> on the corrosion inhibition behaviour of a pre-optimised NBR-PAni.DBSA blend was successfully studied. It was shown that the electrical conductivity of this blend could be enhanced up to a magnitude order (in the region of 10<sup>-2</sup> S.cm<sup>-1</sup>) for TiO<sub>2</sub> contents, 20.0-22.5 wt %. As found from the TEM morphological study, blend with very high content of TiO<sub>2</sub> (25.0 wt %) encountered a more serious phase separation and porosity problem between the NBR host matrix and TiO<sub>2</sub>. From both total immersion and electrochemical corrosion

tests, NBR-PAni.DBSA blends with 20.0-22.5 wt % TiO<sub>2</sub> loadings are deemed to be the best corrosion inhibitor for carbon steel, either in acid or artificial brine environment. This phenomenon is attributed to their better electrical conductivities and also lower phase separation problem between the NBR and TiO<sub>2</sub>.

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