

## Corrosion Protection of Carbon Steel Using Polyaniline Composite with Inorganic Pigments

(Perlindungan Kakisan Keluli Karbon Menggunakan Komposit Polianilin dengan Pigmen Inorganik)

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### ABSTRACT

*Two inorganic pigments ( $TiO_2$  and  $SiO_2$ ) were used to prepare composites with polyaniline (PANI) by situ polymerization method. PANI and PANI composites with  $SiO_2$  and  $TiO_2$  were characterized using Fourier transform infrared spectroscopy and X-ray diffraction. The morphology of the synthesized pigments (PANI, PANI- $SiO_2$  and PANI- $TiO_2$ ) was examined using scanning electron microscopy. Samples were then used as pigments through blending them with acrylic paint and applied on the surface of carbon steel panels. Corrosion was evaluated for coating of carbon steel panels through full immersion test up to standard ASTM G 31. Mass loss was calculated after they have been exposed in acidic media. A digital camera was also used for monitoring corrosion visually on the surface of carbon steel specimens. The results revealed that acrylic paint pigmented by PANI- $SiO_2$  composite was more efficient in corrosion protection for carbon steel compared with the other synthesized pigments.*

*Keywords: Composite pigments; corrosion protection; polyaniline*

### ABSTRAK

*Dua pigmen inorganik  $TiO_2$  dan  $SiO_2$  digunakan untuk menghasilkan komposit dengan polianilin (PANI) dengan kaedah pemolimeran situ. PANI dan PANI komposit dengan ( $SiO_2$ ,  $TiO_2$ ) dicirikan menggunakan spektroskopi transformasi Fourier inframerah dan pembelau sinar-X. Mikroskop elektron imbasan digunakan untuk memerhatikan morfologi pigmen sintesis (PANI, PANI- $SiO_2$  dan PANI- $TiO_2$ ). Sampel kemudian digunakan sebagai pigmen melalui pencampuran dengan cat akrilik dan diterapkan pada permukaan panel keluli karbon. Kakisan dinilai untuk lapisan panel keluli karbon melalui perendaman penuh mengikut piawaian ASTM G31. Kehilangan jisim dikira selepas didedah kepada medium berasid. Kamera digital juga digunakan untuk pemantauan visual kakisan pada permukaan spesimen keluli karbon. Keputusan kajian menunjukkan bahawa cat akrilik berpigmen PANI- $SiO_2$  komposit lebih cekap dalam perlindungan kakisan untuk keluli karbon berbanding dengan pigmen lain yang disintesis.*

*Kata kunci: Perlindungan kakisan; pigmen komposit; polianilin*

### INTRODUCTION

Conductive polymers were widely used as corrosion inhibitor and attracted researchers for use with conventional coatings as anticorrosion pigment. Polyaniline (PANI) is one of the best candidates for enhancing anticorrosion properties of paint due to its environmentally friendly, anticorrosion ability, ease of preparation, excellent environmental stability and interesting in redox properties associated with the nitrogen chain (Kinlen et al. 1997; Lu et al. 1995; Talo et al. 1997; Talo et al. 1999; Wessling & Posdorfer 1999; Wessling 1997). Recently, many researchers improved anticorrosion properties of PANI through composites of PANI with other active pigments such as glass flake which is used with epoxy coatings in marine atmosphere (Sathiyarayanan et al. 2007a). In the organic coating,  $Fe_2O_3$  is widely used in primer coating under organic barrier or as pigment with it.

Polyaniline- $Fe_2O_3$  composite is reported to offer excellent corrosion protection (Sathiyarayanan et al. 2007b). Titanium dioxide is usually used in organic coatings as anticorrosion pigment. Polyaniline- $TiO_2$  composite (PTC) shows efficient performance in organic coating in comparison with PANI alone (Sathiyarayanan et al. 2007c). Besides,  $TiO_2$  with  $SiO_2$  have been used for reinforced organic coating (epoxy) against corrosion (Shi et al. 2008).  $SiO_2$  is practically useful in enhancing organic coating and supports the paint in aggressive environment (Li et al. 2007). Moreover, preparation of polyaniline- $SiO_2$  composite concerned only with electrical activities (Dutta & De 2007) and transport and optical properties (Dutta & De 2006). In this paper, we synthesized and characterized PANI, PANI- $SiO_2$  and PANI- $TiO_2$  and study their anticorrosion performance by immersion tests carried out in acid media.

## MATERIALS AND METHODS

## MATERIALS

Aniline monomer was provided by Mallinckrodt U.S.A. The dopant phosphoric acid ( $\text{H}_3\text{PO}_4$ ) was provided by MERCK Germany, the composite of silicon dioxide ( $\text{SiO}_2$ ) was provided by Emory. Ammonium persulfate (APS) ( $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ) was provided by QRëC Germany. Paint coating (acrylic paint) was provided by Nippon Paint Malaysia. Sodium chloride for immersion test and salt spray was obtained from MERCK Germany.

## CHEMICAL POLYMERIZATION

First, three mixtures of 200 mL of 1M aniline and 1M of phosphoric acid were prepared by mixing for 10 min to allow the aniline monomer to be doped by phosphoric acid before synthesizing PANI (Figure 1). Second, in order to prepare the composites, 2M  $\text{SiO}_2$  and  $\text{TiO}_2$  powders were added in two mixtures of aniline-phosphoric acid separately. After adding the powder to the solution, the mixture was stirred for 30 min to prevent aggregation of the  $\text{SiO}_2$  powder and allowing aniline-phosphoric acid to deposit on surface of the  $\text{SiO}_2$  through the attraction between aniline and the positive charge of inorganic oxides (Kosmulski 2002). Pre-cooled 200 mL of 1M solution of ammonium persulfate was added dropwise to the mixtures for about 2 h with constant stirring. The reaction was conducted at  $5 \pm 1^\circ\text{C}$ . After the ammonium persulfate has dropped completely, the stirring was continued for 4 h to ensure the reaction is complete. A dark green coloured PANI (Figure 1) and the two composites were collected on a Büchner funnel, and washed several times with de-ionized water to remove excess acid content until the filtered substance became almost colourless. The products were dried in a vacuum oven at about  $55^\circ\text{C}$  for 24 h. Finally, the dried product was ground using hand mortar then used as pigments.

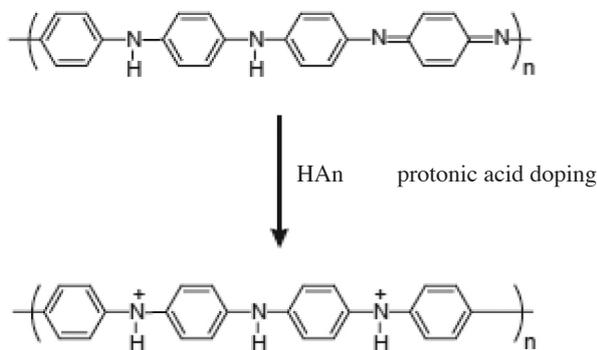


FIGURE 1. PANI doped by phosphoric acid

## INSTRUMENTATIONS

The prepared pigment was characterized by FTIR spectrometer (PerkinElmer) under the range  $4000\text{--}400\text{ cm}^{-1}$ . They were also analyzed by X-ray diffraction method with Siemens D5000 Diffractometer. Scanning electron microscope (SEM) JEOL (JSM-6390LV) was used for morphological examination of the pigments. SF/450/CCT) was used for corrosion evaluation of carbon steel panel coated with modified acrylic paint. Evaluation of corrosion was done by full immersion test based on the calculated mass loss at the end of exposed period. Carbon steel samples were weighed in an electronic balance (Precisa, Model XT220) with an accuracy of 0.1 mg.

## SAMPLES PREPARATION

The coatings were prepared by blending acrylic paint with pigments (PANI, PANI- $\text{SiO}_2$  and PANI- $\text{TiO}_2$ ) using lab attritor for 45 min. The ratio of each pigment was fixed at 15% and acrylic paint at 25% of total volume. The prepared coatings were kept in an air tight jar to avoid any solvent evaporation and the formation of paint gel. Carbon steel samples of circular shape were cut from sheet and not bar stock, to minimize the exposed end grain according to ASTM G31 standard. The samples were polished by fine size emery paper (600 grit), cleaned, degreased with industrial grade acetone, dried and weighed with an accuracy of  $\pm 1\text{ mg}$ . Sample shape and size was made convenient to laboratory corrosion tests according to ASTM G31 standard. Samples with diameter of about 38 mm and thickness of approximately 3 mm, with a hole about 10 mm in diameter were prepared. First the samples were dip coated for 15 s in acrylic paint modified by the three pigments and then left for 1 h to dry; the second dip was for 20 s then dried in an oven for 48 h at  $40^\circ\text{C}$ .

## CORROSION EVALUATION

Immersion test technique is one of corrosion studies used for carbon steel samples, coated with acrylic paint pigmented by synthesized pigments. The total paint system for immersion test was applied on carbon steel samples by, dip technique and allowed to dry for two days in an oven at  $40^\circ\text{C}$ . Carbon steel samples were weighed before coating in an electronic balance (Precisa, Model XT220) with an accuracy of 0.1 mg. After the end of (60 days) immersion test period in 5% sodium chloride solution, the samples were taken out and the coating removed and then the rust was cleaned again according to ASTM G1 standard. The performance of the coating was examined visually and through calculation of the mass loss.

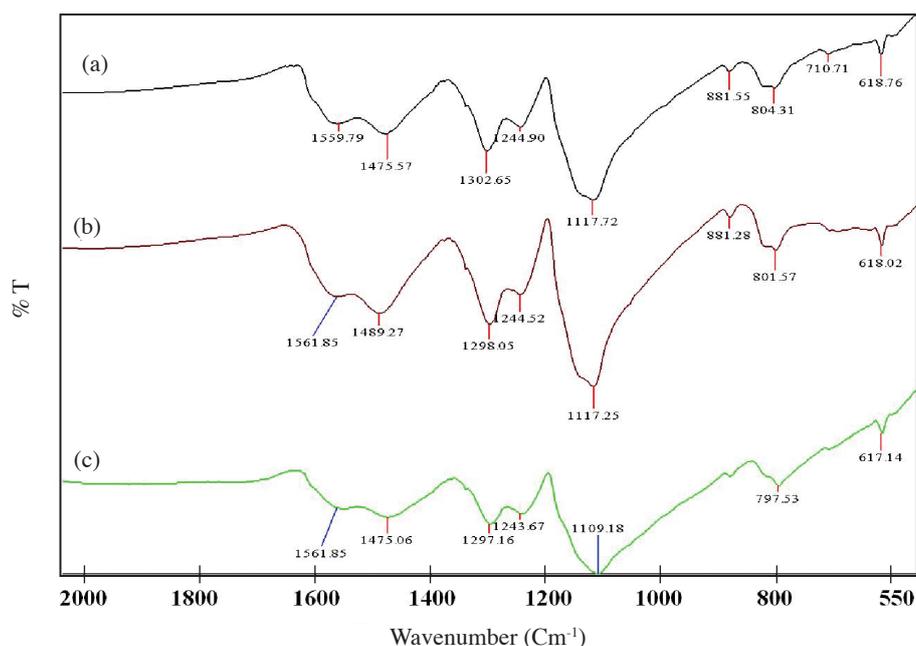


FIGURE 2. FTIR Spectra of pigments (a) PANI, (b) PANI-TiO<sub>2</sub> (c) PANI-SiO<sub>2</sub>

## RESULTS AND DISCUSSION

### FOURIER TRANSFORM INFRARED (FTIR)

The FTIR spectra examination of PANI, PANI-SiO<sub>2</sub> and PANI-TiO<sub>2</sub> revealed that the composites contain all the main characteristics of bands of PANI. Bands at 1560 and 1480 cm<sup>-1</sup> are the stretching mode of C=N and C=C, the bands at 1298 and 1245 cm<sup>-1</sup> are to C-N stretching mode of benzenoid ring and the band at 1117 - 1109 cm<sup>-1</sup> is assigned to a plane bending vibration of C-H mode which is found during protonation (Kang et al. 1998). These peaks when compared to that of pure PANI (Li et al. 2004) are found to be shifted slightly due to strong attraction of TiO<sub>2</sub> particles with PANI (Lee et al. 2005). In the case of TiO<sub>2</sub>, strong absorption around 670 cm<sup>-1</sup> due to Ti-O stretching (Xu et al. 2005) is observed while this band was found to be weak in PANI-TiO<sub>2</sub> due to the presence of PANI. Besides, PANI-SiO<sub>2</sub> and pure PANI are difficult to assign the absorption peaks of the composite because the SiO<sub>2</sub> particles and doped PANI absorb at similar wave numbers. By comparing the two peaks, they have same peaks except peak of C-H at 1117 cm<sup>-1</sup> which was slightly shifted to 1109 cm<sup>-1</sup> due to interaction with SiO<sub>2</sub> particles (Li et al. 2005).

### X-RAY DIFFRACTION

XRD patterns of TiO<sub>2</sub>, SiO<sub>2</sub>, PANI and the composition of PANI with TiO<sub>2</sub>, and SiO<sub>2</sub> suggest some similarity between the two the XRD patterns of two inorganic particles before composited and almost similar to that after composited with PANI. Further, the broad diffraction peak of PANI at 2θ = 25° is absent in the PANI-TiO<sub>2</sub> and SiO<sub>2</sub> which indicates that the presence of TiO<sub>2</sub>, SiO<sub>2</sub> in the polymerization

system strongly affects the crystalline behavior of PANI form and the interaction of PANI with TiO<sub>2</sub> and SiO<sub>2</sub> narrowing the crystallization of PANI. This indicates that PANI deposited on the surface of particles has no effect on the crystalline structure of TiO<sub>2</sub>, and SiO<sub>2</sub>. Besides, these results indicate that PANI is amorphous in the PANI-Fe<sub>2</sub>O<sub>3</sub> composite since the molecular chain of the adsorbed PANI is confined and the degree of crystallinity is decreased (Sathiyarayanan et al. 2007b).

It also confirmed that the PANI deposited on the surface of particles has no effect on the crystallization behavior of TiO<sub>2</sub>, SiO<sub>2</sub> particles. Beside, the XRD pattern for PANI-TiO<sub>2</sub> composites (Figure 3) were similar after comparing it with previous reports (Lee et al. 2005; Sathiyarayanan et al. 2007c).

### SCANNING ELECTRON MICROSCOPY (SEM)

The scanning electron micrographs of PANI TiO<sub>2</sub>, and SiO<sub>2</sub> alone and modified with PANI are shown in Figure 4. It can be seen that spherical shape of large sized crystals of TiO<sub>2</sub> and PANI appear in the samples. The core TiO<sub>2</sub> particles are fully shelled by PANI in the case of PANI-TiO<sub>2</sub> (Li et al. 2008; Li et al. 2003; Yavuz & Gök 2007). Also the flake like particles of SiO<sub>2</sub> will be covered by the polyaniline spheres which is deposited and encapsulated the surface of SiO<sub>2</sub> particles (Figure 4).

### FULL IMMERSION TEST

Figure 5 shows the influence of aggressive media on samples at the end of exposing period. Table 1 shows the values of the mass lost from carbon steel samples during the immersion test. The pigments efficiency against corrosion can be estimated from Figure 6. The results revealed that

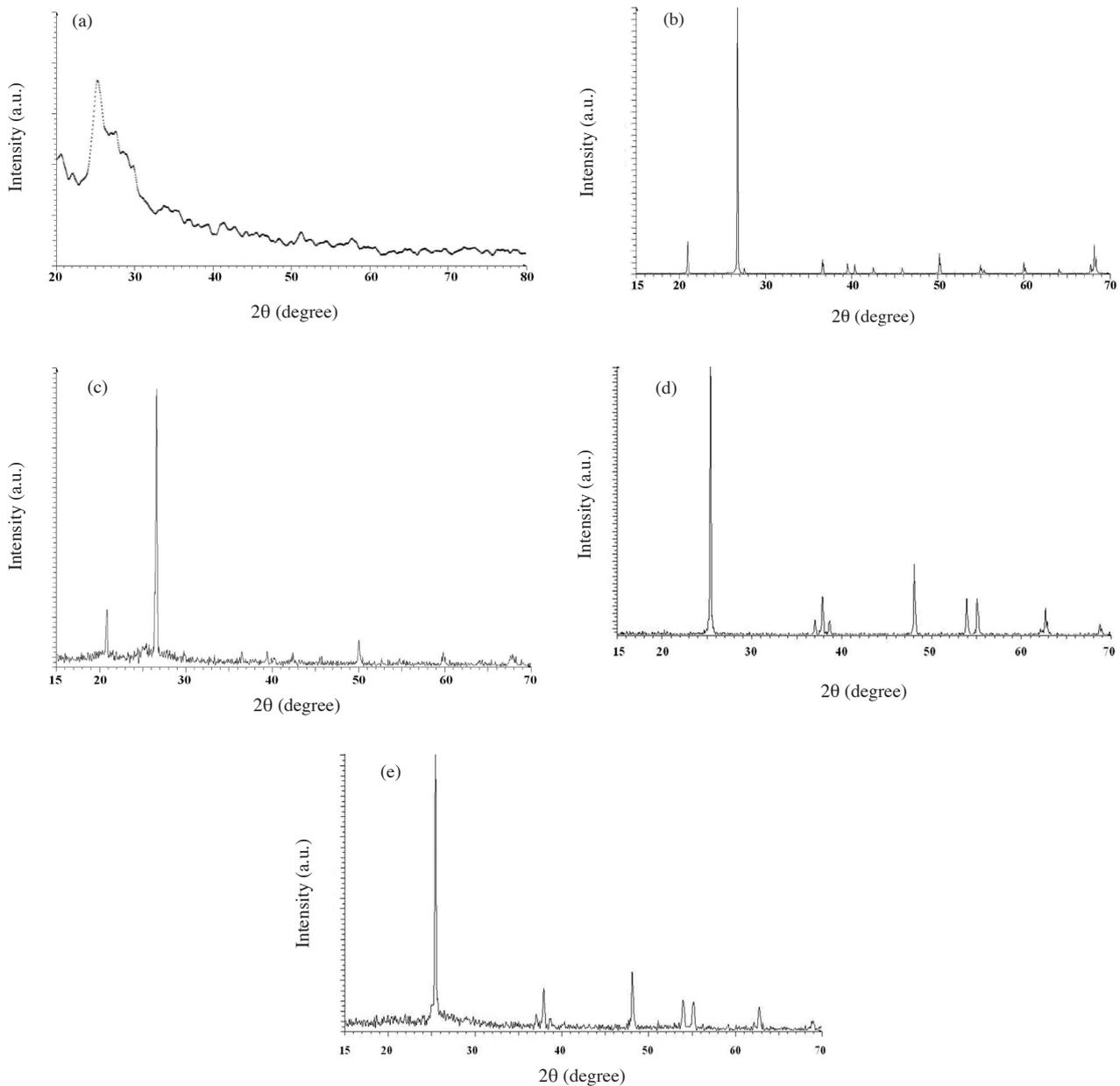


FIGURE 3. XRD patterns for pigments before and after composite (a) PANI, (b)  $\text{SiO}_2$ , (c) PANI- $\text{SiO}_2$ , (d)  $\text{TiO}_2$  and (e) PANI- $\text{TiO}_2$

composite pigments with PANI is more protectable to steel sample than only PANI. Acrylic coating pigmented PANI- $\text{SiO}_2$  had the lowest mass loss.

#### CONCLUSION

In this work PANI, PANI- $\text{TiO}_2$  and PANI- $\text{SiO}_2$  composites were prepared by situ-polymerization technique and used as anticorrosive pigment in acrylic paint system for application on carbon steel samples. The pigments were characterized by FT-IR, XRD and SEM. Anticorrosion ability of the coating were evaluated by immersion test using 5% sodium chloride solution and weight loss method.

Polyaniline- $\text{SiO}_2$  composite pigment containing paint showed the best results in terms of corrosion protection of the carbon steel samples.

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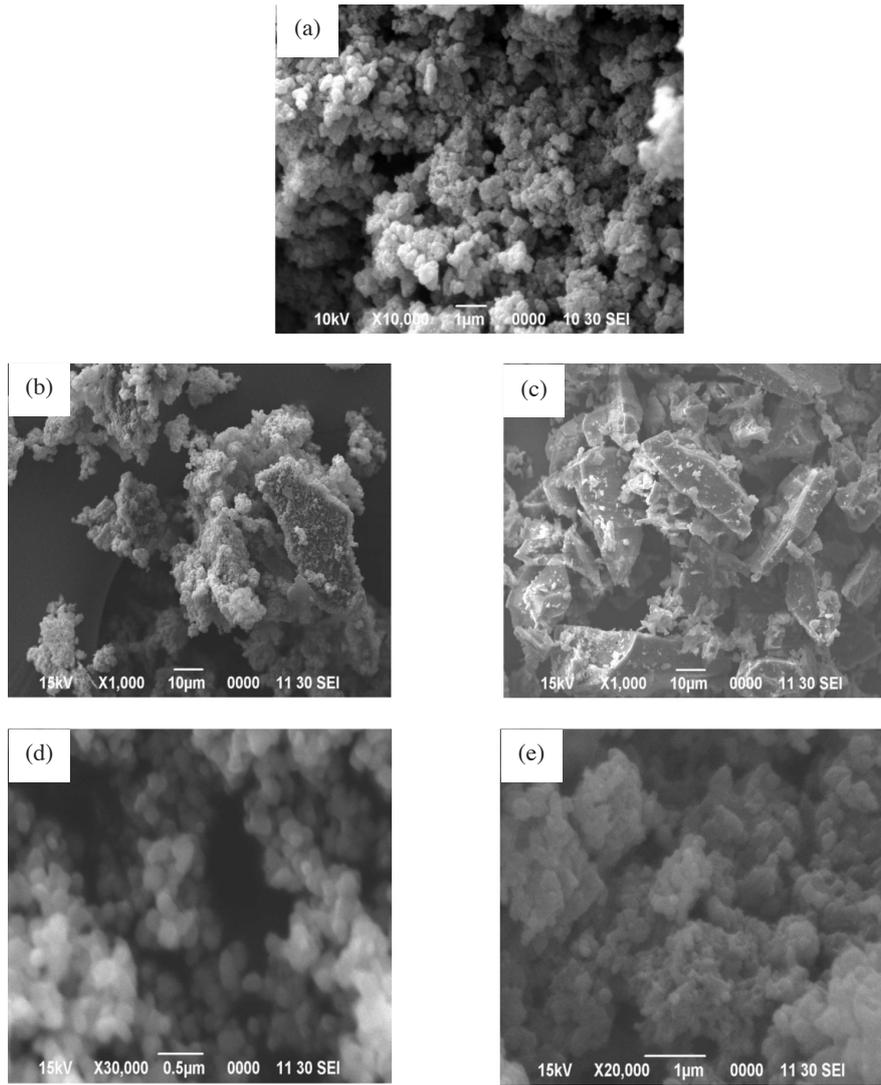


FIGURE 4. SEM for pigments before and after composite (a) PANI, (b) SiO<sub>2</sub>, (c) PANI-SiO<sub>2</sub>, (d) TiO<sub>2</sub> and (e) PANI-TiO<sub>2</sub>

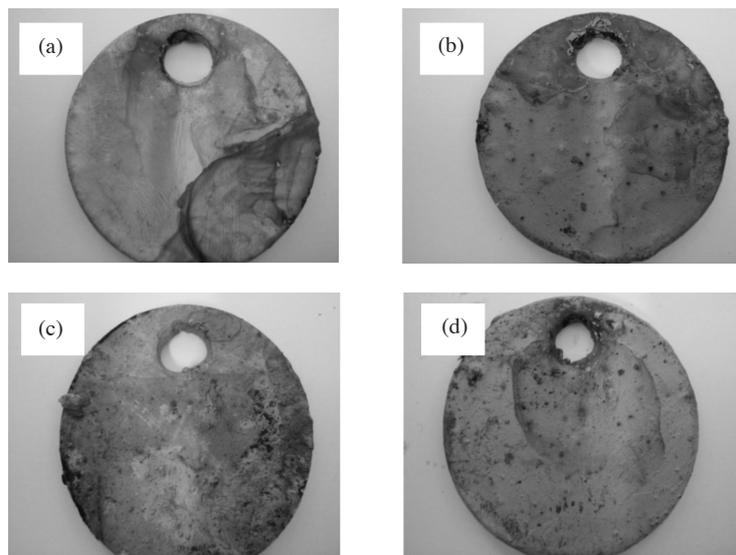


FIGURE 5. Samples after 60 days fully immersion test in 5% NaCl (a) pain alon, (b) PANI alon, (c) PANI- TiO<sub>2</sub> and (d) PANI-SiO<sub>2</sub>/PANI alon

TABLE 1. Mass loss

Paint systems	Samples weights before test (g)	Sample weights after test (g)	Average values of mass loss (g)
Paint alone	20.252	20.0908	0.1612
Paint modified with PANI	20.326	20.1898	0.1362
Paint modified with PANI-TiO <sub>2</sub> composite	20.294	20.1720	0.1220
Paint modified with PANI-SiO <sub>2</sub> composite	20.284	20.1639	0.1201

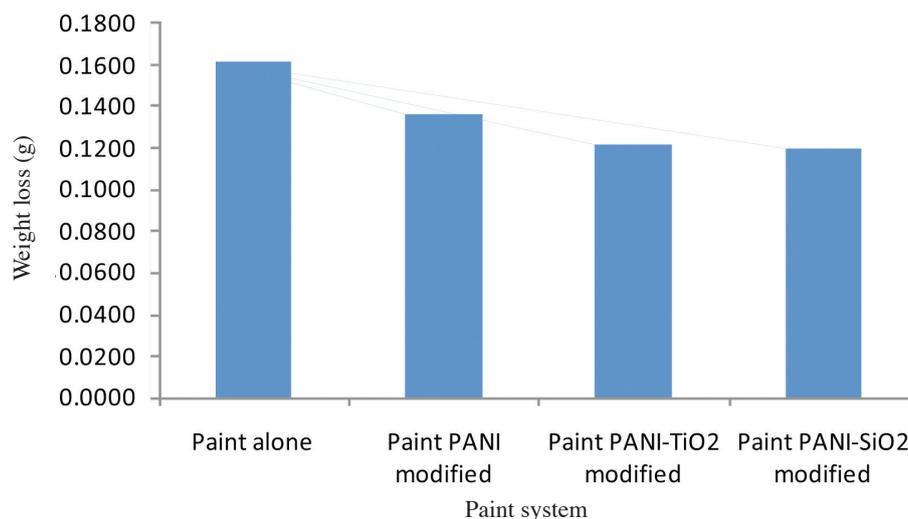


FIGURE 6. Mass loss for different systems coated steel panels

## REFERENCES

- Dutta, K. & De, S. K. 2006. Transport and optical properties of SiO<sub>2</sub>-polypyrrole nanocomposites. *Solid State Communications* 140: 167-171.
- Dutta, K. & De, S.K. 2007. Optical and electrical characterization of polyaniline-silicon dioxide Nanocomposite. *Physics Letters A*. 361: 141-145.
- Kang, E.T., Neoh, K.G. & Tan, K.L. 1998. Polyaniline: a polymer with many interesting intrinsic redox states. *Progress in Polymer Science* 23: 277-324.
- Kinlen, P.J., Silverman, D. & Jeffreys, C.R. 1997. Corrosion protection using polyaniline coating formulations. *Synthetic Metals* 85: 1327-1332.
- Kosmulski, M. 2002. The significance of the difference in the point of zero charge between rutile and anatase. *Advances in Colloid and Interface Science* 99: 255-264.
- Lee, I.S., Lee, J.Y., Sung, J.H. & Choi, H.J. 2005. Synthesis and electrorheological characteristics of polyaniline-titanium dioxide hybrid suspension. *Synthetic Metal* 152: 173-176.
- Li, H., Zhang, Z., Ma, X., Hu, M., Wang, X. & Fan, P. 2007. Synthesis and characterization of epoxy resin modified with nano-SiO<sub>2</sub> and  $\gamma$ -glycidoxypropyltrimethoxy silane. *Surface & Coatings Technology* 201: 5269-5272.
- Li, X., Chen, W., Bian, C., He, J., Xu, N. & Xue, G. 2003. Surface modification of TiO<sub>2</sub> nanoparticles by polyaniline. *Applied Surface Science* 217: 16-22.
- Li, X., Wang, G. & Li, X. 2005. Surface modification of nano-SiO<sub>2</sub> particles using polyaniline. *Surface & Coatings Technology* 197: 56-60.
- Li, X., Wang, G., Li, X. & Lu, D. 2004. Surface properties of polyaniline/nano-TiO<sub>2</sub> composites. *Applied Surface Science* 229: 395-401.
- Li, X., Wang, D., Luo, Q., An, J., Wang, Y & Cheng, G. 2008. Surface modification of titanium dioxide nanoparticles by polyaniline via an *in situ* method. *Journal of Chemical Technology and Biotechnology* 83: 1558-1564.
- Lu, W., Elsenbaumer, R.L. & Wessling, B. 1995. Corrosion Protection Of Mild Steel By Coatings Containing Polyaniline. *Synthetic Metals* 71: 2163-2166.
- Sathiyarayanan, S., Azim, S.S. & Venkatachari, G. 2007c. Preparation of polyaniline-TiO<sub>2</sub> composite and its comparative corrosion protection performance with polyaniline. *Synthetic Metals* 157: 205-213.
- Sathiyarayanan, S., Syed Azim, S. & Venkatachari, G. 2007a. Corrosion protection coating containing polyaniline glass flake composite for steel. *Electrochimica Acta* 53: 2087-2094.
- Sathiyarayanan, S., Syed Azim, S. & Venkatachari, G. 2007b. Preparation of polyaniline-Fe<sub>2</sub>O<sub>3</sub> composite and its anticorrosion performance. *Synthetic Metals* 157: 751-757.
- Shi, H., Liu, F., Yang, L. & Han, E. 2008. Characterization of protective performance of epoxy reinforced with nanometer-sized TiO<sub>2</sub> and SiO<sub>2</sub>. *Progress in Organic Coatings* 62: 359-368.
- Talo, A., Forsen, O. & Ylasaari, S. 1999. Corrosion protective polyaniline epoxy blend coatings on mild steel. *Synthetic Metals* 102: 1394-1395.

- Talo, A., Passiniemi, P., Forsen, O. & Ylasaari, S. 1997. Polyaniline/Epoxy Coatings with Good Anti-Corrosion Properties. *Synthetic Metals* 85: 1333-1334.
- Wessling, B. 1997. Scientific Commercial Breakthrough for Organic Metals. *Synthetic Metals* 85: 1313-1318.
- Wessling, B. & Posdorfer, J. 1999. Polyaniline/epoxy coatings with good anti-corrosion properties. *Synthetic Metals* 102: 1400-1401.
- Xu, J., Liu, W. & Li, H. 2005. Titanium dioxide doped polyaniline. *Materials Science and Engineering: C*. 25: 444-447.
- Yavuz, A.G. & Gök, A. 2007. Preparation of TiO<sub>2</sub>/PANI composites in the presence of surfactants and investigation of electrical properties. *Synthetic Metals* 157: 235-242.

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