

IMPROVING THE ANTI-CORROSION PROPERTIES VIA SURFACE MODIFICATION FOR SILICON DIOXIDE BY CONDUCTIVE POLYMER

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ABSTRACT

The modification of silicon dioxide surface via polyaniline (PANI) prepared by in-situ polymerization method. PANI and PANI-SiO₂ were characterized using Fourier transform infrared; X-ray diffraction and digital multimeter was used to measure conductivities for samples. Morphology of the synthesized PANI and PANI-SiO₂, were examined using scanning electron microscopy. Samples were then used as pigments through blended 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, salt spray test and adhesion test up to standards; ASTM G 31, ASTM B117 and ASTM D3359 respectively. Corrosion rate and coating adhesion were calculated after finished exposed periods in acidic Medias. Digital camera also used for monitored corrosion visually on the surface of carbon steel specimens. The results revealed that acrylic paint pigmented by SiO₂ modified by polyaniline, more efficiently in corrosion protection for carbon steel than each of PANI and SiO₂.

Keywords: Surface modification, Conductive polymers, Polyaniline, Corrosion inhibition

1. INTRODUCTION

Conductive polymers are widely used as corrosion inhibitor, aesthetically attracted researchers when being used with conventional coatings as anti-corrosion pigment. PANI is one of the best candidates for enhancing anti-corrosion properties of paint due to; its environmentally friendly, anti-corrosion ability, ease of preparation, excellent environmental stability and interesting in redox properties associated with the nitrogen chain (Talo et al., 1999 and Wessling and Posdorfer, 1999). Recently, surface modification of active pigments by conductive polymer, is one of the common methods to improve anti-corrosion properties. PANI modified of glass flack is used to enhance epoxy coating in marine environments (Sathiyarayanan et al., 2007a). Fe₂O₃ and Al₂O₃ modified by PANI showed an excellent result as corrosion inhibitor (Sathiyarayanan et al., 2007b and Al-Dulaimi et al., 2011). On the other hand, Titanium dioxide (TiO₂) in powder form was reported to promote performance of coatings against corrosion (Zhang et al., 2007). Besides, SiO₂ in powder form enhanced effectively the toughness and thermal stability of organic coating (Zhang et al., 2006). Moreover, TiO₂ modified by PANI shows excellent

properties in terms of electrical conductivity, thermal stability and spectroscopic characteristics (Li et al., 2008a; Li et al., 2003 and Lee et al., 2005) and efficient performance in organic coatings compared with PANI alone (Sathiyarayanan et al., 2007c). However, previous studies of SiO₂ modified by PANI only focused on their electrical and optical properties and dispersion stability (Dutta and De, 2007; Li et al., 2008b and Li et al, 2005). Surface modification is the one of the recent techniques to improve the surface properties for various materials and access unique properties via new hybrid materials (Nora'aini et al., 2011 and Ndaliman et al., 2011).

For the best of the authors' knowledge, the application of SiO₂ modified by PANI as Anti-corrosion pigment has not reported yet; which is the major objective of the present paper. This study describes the process of synthesizing and characterizing of PANI and SiO₂ modified by PANI and the evaluation of their anti-corrosion performance using fully immersion test and salt spray test carried out in acidic media.

2. MATERIALS AND METHODS

2.1 Materials

Aniline monomer was provided by Mallinckrodt U.S.A, the dopant phosphoric acid (H₃PO₄) was provided by MERCK Germany, the composite of silicon dioxide (SiO₂) was provided by Emory. Ammonium persulfate (APS) (NH₄)₂S₂O₈ provided by QRëC Germany, acrylic paint, paint coating (Nippon paint), sodium chloride (NaCl) for immersion test and salt spray was obtained from MERCK Germany and carbon steel plates were provided from university mechanical lab.

2.2 Chemical polymerization

200 ml of solution containing deionized water with 1 mole aniline doped by 1 mole of phosphoric acid. The mixture was prepared via mixed for 10 minis to allow the aniline monomer doped by phosphoric acid before starting synthesise of PANI (Figure 1). 2 mole of SiO₂ powder was added to (aniline-Phosphoric acid) mixture in order to modify SiO₂ surface. After added the powder to the solution, the mixture was stirred for 30 minutes to prevent aggregation of the SiO₂ powder and allowing to the (aniline-Phosphoric acid) deposit on surface of the SiO₂ through the attraction between aniline and the positive charge of SiO₂ (Kosmulski, 2002). Pre-cooled 200 ml of 1 mole solution of initiator ammonium

persulfate was added dropwise to the pre-cooled (aniline-acid) and (SiO₂-aniline-acid) mixtures for about 2 hours with constant stirring. The reaction was conducted at 5±1 °C. After dropped ammonium persulfate completely, the stirring was continued for 4 hours to ensure completion of reaction. A dark green colored PANI (Figure 1) and SiO₂ modified by PANI (Figure 2) was collected on a Büchner funnel, and then washed several times with de-ionized water to remove excess acid content until the filtered substance was became almost colorless. The PANI-SiO₂ was dried in a vacuum oven at about 55 °C for 24 hours. Finally, the dried product was grinded using hand mortar then used as pigment.

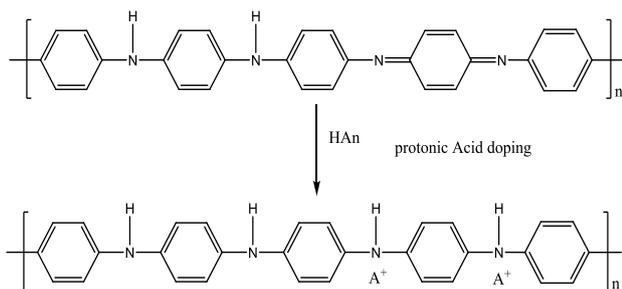


Figure 1 PANI doped phosphoric acid

2.3 Instrumentation

The prepared pigment was characterized by FTIR spectrometer (PerkinElmer) under the range 4000–400 cm⁻¹. They were also analyzed by X-ray diffraction method with Siemens (Diffraktometer D5000) X-ray. Conductivity was measured on compressed pellets of the powder sample by the digital Multimeter (CP7676 Actron) at 25 °C. Scanning electron microscopy (SEM) JEOL (JSM-6390LV) was used for morphological examination of the pigments. Salt spray cabinet (Cyclic corrosion cabinet model. SF/450/CCT) was used for corrosion carbon steel panel coated acrylic paint modified. Evaluated corrosion by fully immersion test based on calculates mass loss after the end of exposed period. Carbon steel samples were weighed in an electronic balance (Precisa, Model XT220) with an accuracy of 0.1 mg.

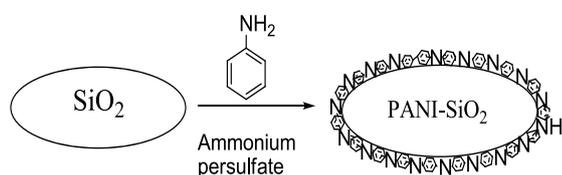


Figure 2 Preparation of PANI-SiO₂ composite

2.4 Samples preparation

The coatings were prepared by blending of acrylic paint with pigments (PANI, SiO₂ and PANI-SiO₂) using lab attritor for 45 minutes. The ratio of each pigment (PANI, SiO₂ and PANI-SiO₂) was fixed 15% and acrylic paint 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 (600grit), cleaned, degreased with industrial grade acetone, dried and weighed with an accuracy of ± 1 mg. Samples shape and size is a convenient to laboratory corrosion tests according to ASTM G31standard. Samples diameter about 38 mm and thickness of approximately 3 mm, hole was made in every sample about 10 mm in diameter. First the samples were dip coated for 15 seconds in acrylic paint modified by the three pigments then left for 1 hour to dry, second dip for 20 seconds then dried in an oven for 48 hours at 40°C. Beside, coatings evaluated by salt spray technique according to ASTM B117 standard. The required test panels, length 127 mm, width 76 and thickness of approximately 0.8 mm. Carbon steels samples were coated by hand brush for two layers. Samples left to dry for 48 hours then made special crack in coating with concern for the depth and length to be similar for the four samples.

2.5 Evaluation of coating

Immersion test technique was one of corrosion studies for carbon steel samples, which were coated by 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°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, samples were taken out and removed the coating then cleaned the rust again according to ASTM G1 standard. The performance of the coating was examined visually and through calculating the corrosion rate according to Eq. (1) in ASTM G31 standard.

$$\text{Corrosion Rate} = \frac{K.W}{A.T.D} \quad (1)$$

K = a constant

T = time of exposure

A = area

W = mass loss

D = density

In addition to full immersion tests, salt spray test is another technique for evaluation of coating according to ASTM B117 standard. The pigmented acrylic paint was applied on the surface of carbon steel samples using brush. Then samples were exposed in salt spray chamber for 35 days. Corrosion was evaluated after end of an exposed period through visually observation and tested adhesion strength for coating using pull up tape according to ASTM D3359 standard.

3. RESULTS AND DISCUSSION

3.1 Fourier transform infrared (FTIR)

The FTIR spectra examination of PANI and PANI-SiO₂ (Figure 3) revealed that; the PANI composite contains

the same main characteristics of bands to pure PANI. Bands around 1600 cm^{-1} (Tang et al., 1988) and 1500 cm^{-1} (Cao et al., 1986) were assigned to the stretching mode of C=N and C=C bonds, the bands around 1300 cm^{-1} and 1250 cm^{-1} (Sathiyarayanan et al., 2007d) were assigned to the stretching mode of benzenoid ring to C-N bond and the band at 1117 cm^{-1} was assigned to a plane bending vibration of C-H mode which is found during protonation (Kang et al., 1998). The SiO_2 modified by PANI, the spectrum in Figure 3 showed that composite contain all the main characteristics of bands of PANI except peak for C-H around 1115 cm^{-1} . These peaks when compared to that of pure PANI are found to be slightly shifted (Li et al., 2005) might be affected by the interaction of hydrogen bond with oxygen in SiO_2 (Li et al., 2008b).

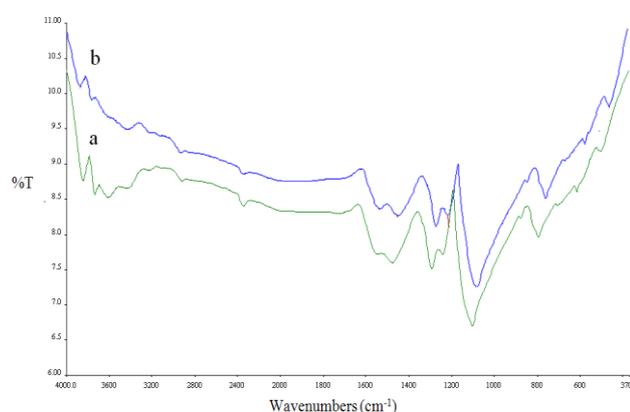


Figure 3 FTIR spectra of PANI and SiO_2 modified by PANI (a) PANI (b) PANI- SiO_2

3.2 X-Ray diffraction (XRD)

The broad diffraction peak of PANI at $2\theta = 25^\circ$ (Figure 4a) indicate that PANI was an amorphous before the composition with SiO_2 (Li et al., 2005). XRD patterns of SiO_2 and PANI- SiO_2 composite (Figure 4 b, c) showed the similarity between the two patterns which is demonstrably that PANI deposited on the surface of SiO_2 particles has no effect on the crystalline structure of SiO_2 . However, the broad diffraction peak of PANI at $2\theta = 25^\circ$ was absent in the PANI- SiO_2 which indicates that the presence of SiO_2 in the polymerization system strongly affects the crystalline behavior of PANI and the interaction of PANI with SiO_2 narrows the diffraction peak of PANI. Similar observations on the XRD pattern after composite has been reported by Sathiyarayanan about PANI modify TiO_2 (Sathiyarayanan et al., 2007c and Sathiyarayanan et al., 2007d)

3.3 Scanning electron microscopy (SEM)

SEM of SiO_2 and SiO_2 -PANI composites (Figure 5) revealed that SiO_2 flack shape of large particles crystals was encapsulated by PANI nanoparticles, which were deposited on the surface of SiO_2 like core shell (Figure 2). The surface charge of a metal oxide such as SiO_2 is positive below the pH of the point of zero charge (PZC) at pH 6, while it is negative above it (Kosmulski, 2002). Aniline monomer doped with H_3PO_4 adsorbed to

compensate positive charge of SiO_2 surface. Therefore, after synthesized PAN showed in (Figure 5c) shield SiO_2 particles.

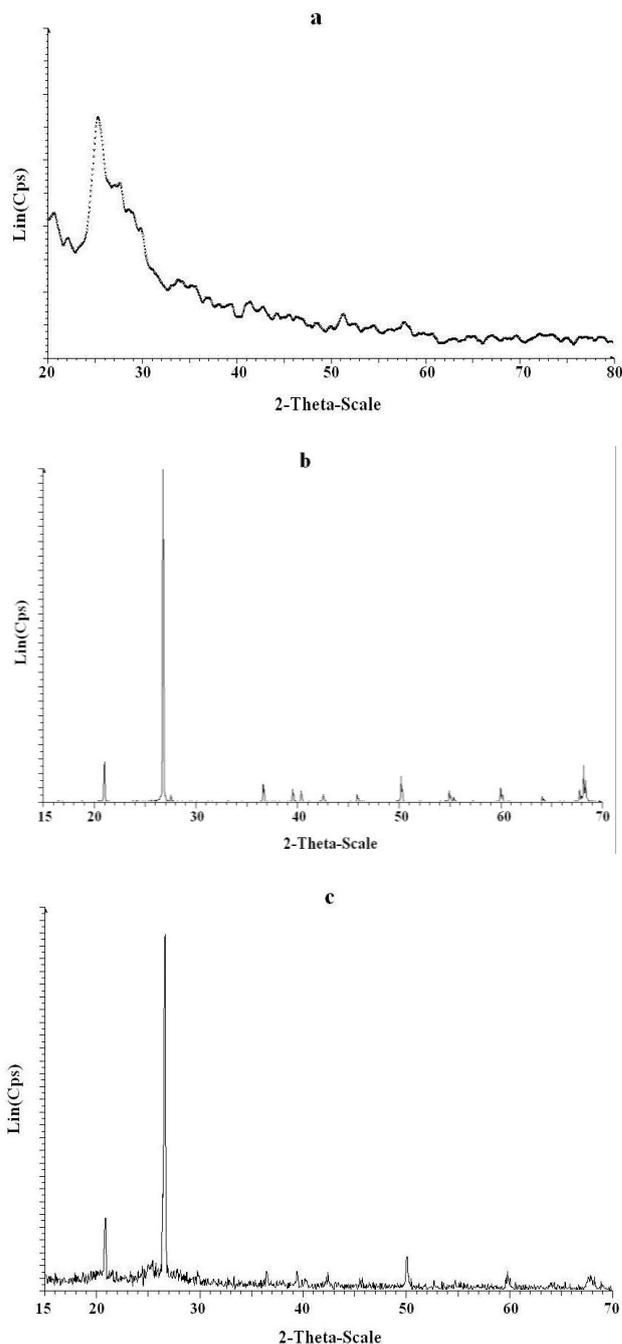


Figure 4 XRD for the three pigments; (a) PANI, (b) SiO_2 and (c) SiO_2 modified by PANI

3.4 Pigment conductivity

The conductivities of the three pigments were measured via digital Multimeter through measured the resistances then converted to value of conductivity by Eq. (2). The powders were pressed into a pellet of 1.29 cm diameter and 0.19 cm thickness under pressure. The conductivity measurement of pigments pellets was measured at room temperature. PANI- SiO_2 composite has the highest conductivity due to the presence of SiO_2

particles has enhanced the conjugations properties to polyaniline. (Figure 6).

$$\text{Conductivity (S/cm)} = \frac{1}{\text{Resistance}(\Omega)} / \text{diameter (cm)} \quad (2)$$

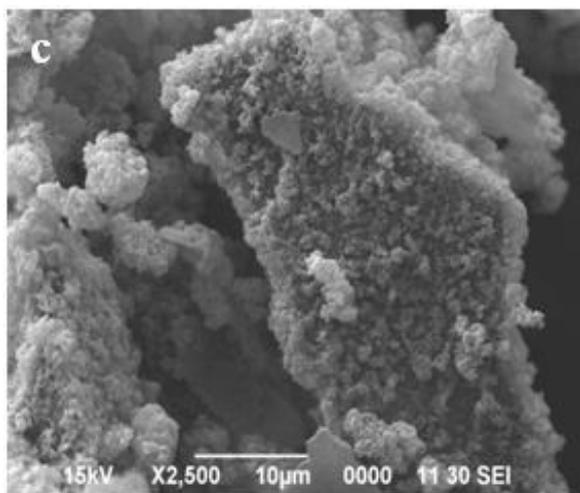
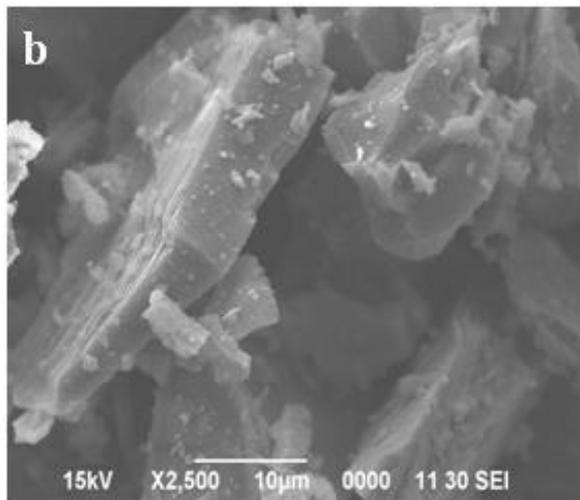
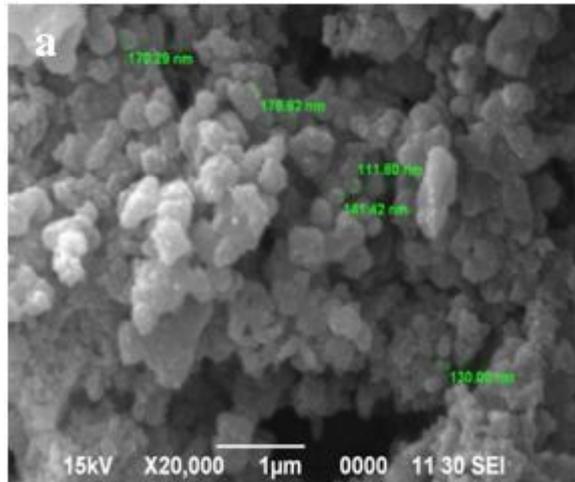


Figure 5 SEM of (a) PANI, (b) SiO₂ before modification with PANI (c) SiO₂ after modification with PANI

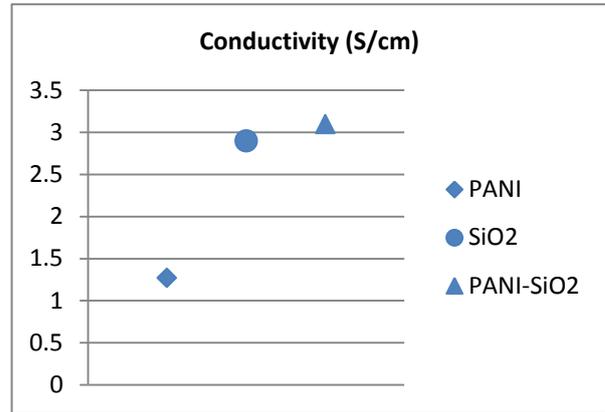


Figure 6 Pigments conductivities

3.5 Corrosion evaluation

3.5.1 Full immersion test

Figure 7 showed the surfaces of samples affected by aggressive environment after end of exposed periods. After measured the weight for the samples, corrosion rate was calculated (Table 1) and the results indicated that PANI-SiO₂ composite was the best corrosion inhibitor among the three samples.

Table 1 Mass loss and corrosion rate

Paint system	Average value of mass loss (g)	Corrosion rate (g/m ² ·h)
Paint modified with SiO ₂	0.048	0.333
Paint modified with PANI	0.049	0.34
Paint modified with PANI-SiO ₂	0.025	0.17

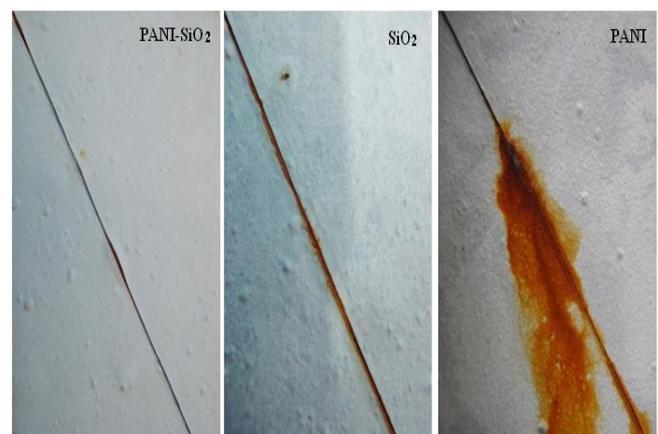


Figure 7 Samples after 35 days of salt spray testing

3.5.2 Salt spray test

According to ASTM B117 standard, three coated specimens were exposed in salt spray chamber for 35 days. Visually we can distinguish pigments Efficiency, through prevention of coatings for carbon steels panels

against corrosion in aggressive environment. The results reveal that coating containing PANI-SiO₂ composite pigments protect carbon steels more efficiently than the other two pigments. Carbon steel coated by acrylic paint pigmented by PANI-SiO₂ composite, was the less sample affected by aggressive environment. might be due to ; either high conductivity for PANI-SiO₂ which supports the pigment to absorbing the aggressive ions or the physical form for PANI-SiO₂, SiO₂ flakes shapes was encapsulated by PANI after completed surface modification (Figure 8). PANI deposited on SiO₂ particles surface impeding the permeability of aggressive ions to the substance (Denise et al., 2007).

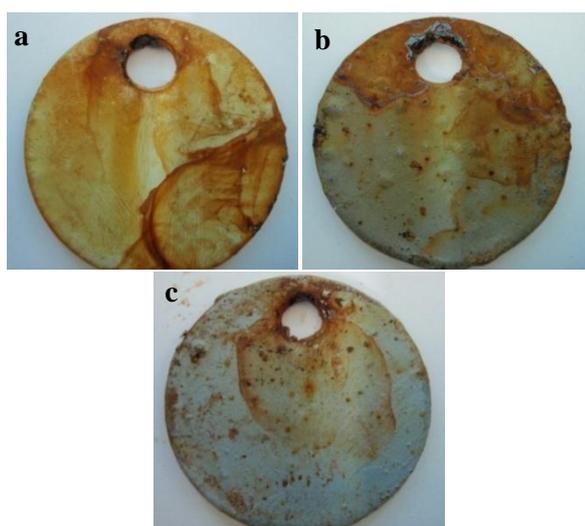


Figure 8 Samples after 60 days fully immersion test (a) acrylic paint containing SiO₂, (b) acrylic paint containing PANI, (c) acrylic paint containing SiO₂ modified by PANI

3.5.3 Adhesion test

After the 35 days of exposure period, adhesion test was carried out according to ASTM D3359 standard using method B (the higher value of adhesion is 5B and the lower one was 0B were given in Table 2. Coating thickness measured according to ASTM D1186 standard and the average of lower and higher thickness had been listed in Table 2. Adhesion and thickness tests were carried out at STATUS HEAD Company (Johor-Malaysia).

The coating adhesion was measured through made a seven liner cracks in horizontal direction Intersected with another seven vertical cracks in order to, produce thirty-six squares in the coatings. These squares were pull it up by special tape with proper motion. coating containing SiO₂ and PANI-SiO₂ pigments had 5B value of adhesion test (none of the squares of the lattice is detached) while coating containing PANI pigment had 4B value of adhesion test (less than 5% of the area is affected).The authors assumes that the decreased in adhesion strength is due to the bad corrosion protection of coating, which means that rust produced between the surfaces, in turn this caused of delamination the coating which causes to

decrease in the adhesion value (Zarras et al., 2003 ; Armelin et al., 2008).

Table 2 Average coating thickness and adhesion test

Pigment	Lower thickness	Higher thickness	Average of adhesion test
PANI	238	292	4B
SiO ₂	246	339	5B
SiO ₂ -PANI	234	293	5B

4. CONCLUSION

In this work, PANI, and SiO₂ modified by PANI composite were prepared by situ-polymerization technique and were used as anticorrosive pigment in acrylic paint system for application on carbon steel samples. The pigments were characterized by FTIR, XRD and SEM. Anticorrosion ability of the coating was evaluated by full immersion test using 5% sodium chloride solution and calculating the average weight loss method in order to calculate the corrosion rate. The surface modification of SiO₂ by PANI positively affected in paint system and showed the best results in terms of corrosion protection of the carbon steel samples.

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