Preparation of polyaniline–Fe$_2$O$_3$ composite and its anticorrosion performance

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Abstract

Polyaniline–Fe$_2$O$_3$ composites were chemically prepared by oxidative polymerization of aniline in phosphoric acid medium with ammonium persulphate as oxidant. Different ratios of aniline–Fe$_2$O$_3$ were taken to prepare polyaniline–Fe$_2$O$_3$ composites, i.e. 1:2, 1:1, 2:1. The composites were characterized by FTIR, XRD and SEM. Using the prepared composites, primer paints with acrylic binder were prepared and coated on the steel samples. The corrosion protection ability of the coating was found out by EIS method in 3% NaCl solution. It has been found that the coating with composite of 1:1 ratio of aniline:Fe$_2$O$_3$ is found to offer higher protection than the coating with other ratios and plain Fe$_2$O$_3$.

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1. Introduction

Organic coatings are widely used for corrosion protection of metals. Most of the primer coatings contain iron oxide (Fe$_2$O$_3$) as one of the pigment. Several studies [1–26] have shown that polyaniline containing organic coatings offer efficient corrosion protection of steel. Coatings containing polyaniline have been shown to protect steel at pinhole and scratches [9,12]. It has been reported that polyaniline containing coatings protect steel by forming a passive layer on the iron surface [5,16,21]. Hence, it is envisaged that polyaniline-coated iron oxide containing coatings can exhibit better corrosion protection ability of iron. Earlier studies on polyaniline–Fe$_2$O$_3$ composites were mostly concerned with their conductivity and magnetic properties [27,28]. Therefore, PANI coated Fe$_2$O$_3$ composites were prepared by in situ polymerization and examined their corrosion protection performance of steel. The results of the study are presented in this paper.

2. Experimental

2.1. Materials

Aniline (A.R.) and ammonium persulphate (A.R.) both were obtained from Sd-Fine Chemicals (India). The monomer was distilled over zinc dust and was kept in dark prior to use. The commercially available iron oxide pigment with particle size of 2–3 μm was used.

2.2. Preparation of PANI–Fe$_2$O$_3$ composites

One molar of distilled aniline was dissolved in 500 ml of 1M solution of phosphoric acid and the required quantity of Fe$_2$O$_3$ was added to it. The mixture was stirred well. Pre-cooled 500 ml of 1M solution of ammonium persulfate was added drop wise to the pre-cooled aniline–acid–Fe$_2$O$_3$ mixture for about 1.5 h with constant stirring. The reaction was conducted at 5 ± 1 °C. After the addition, the stirring was continued for 2 h for ensuring complete polymerization. A dark green coloured PANI–Fe$_2$O$_3$ composite thus formed was filtered and repeatedly washed with distilled water to remove excess acid content. The polymer composite was dried in oven at about 80 °C for 2 h. The polymer composites of different ratios of aniline:Fe$_2$O$_3$, i.e. 1:2, 1:1 and...
were prepared. The dried PANI–Fe₂O₃ composite (PFC) was fine ground using mortar and then used as pigment.

The point of zero charge of Fe₂O₃ is reported to be around 7.2 [29,30]. Hence, it may be positively charged in the H₃PO₄ bath. Due to this, the H₂PO₄⁻ ions adsorb on Fe₂O₃ and this adsorbed ions can work as charge compensator for positively charged PANI chain in the formation of polyaniline–Fe₂O₃ composite. Similar mechanism has been reported for the synthesis of PANI–MnO₂ composite [31].

**2.3. Characterization of PANI–Fe₂O₃ composites (PFC)**

The infrared spectra of the polymer composite were recorded on NICOLET 380 FTIR spectrometer in KBr medium at room temperature in the region of 2000–500 cm⁻¹. X-ray diffraction pattern of PANI–Fe₂O₃ composites were taken with Analytical (Model PW3040/60) X-ray diffractometer using Cu Kα radiation in the 2θ range 0–90° at the scan range of 0.0170° 2θ with continuous scan type with scan step time of 15.5056 s. The morphology of the composites was analyzed using Hitachi (Model S3000 H) scanning electron microscopy by spreading the composite over a copper block over which gold was sputtered. The electrical conductivity of the composite was found by four probe resistivity meter.

**2.4. Preparation of PANI–Fe₂O₃ composite (PFC) containing paint**

The primer is formulated using commercial acrylic resin (Kondicyrl 166, Pidilite, India). The volume solids of the formulation was kept at 30% with 35% pigment volume concentration (P.V.C.). The main pigments used in this formulation were polyaniline, titanium-di-oxide and PFC along with mica and silica as extender pigments. Di-octyl-phosphate (D.O.P.) was used as a plasticizer.

The pigments were pre-mixed and the paint was prepared in a lab attritor. The attritor was run for 45–50 min. The fineness of dispersion of paint was found using Hegmann gauge and it was found to be between 7 and 8. The paint was stored in an air tight container. The specific gravity of the paint was 1.0. The dry film thickness (DFT) of the coating was measured by Minitest thickness meter (Model 600, Electrophysick). The adhesion of the coating was tested by Tape test as per ASTM D3359-02 and found to pass the test.

**2.5. Evaluation of corrosion resistant properties of the coating by EIS studies**

Steel specimens of size 5 cm x 5 cm x 0.1 cm were sandblasted (SA 2.5) and degreased with trichloroethylene and coated with the developed paint. The total thickness of the coating was 40 ± 2 µm. A glass tube of 1.2 cm diameter of length 3 cm was fixed on the coated steel with adhesive (m seal) and the exposed area was 1.0 cm² to the solution. The solution of 3% NaCl was taken in the glass tube. A platinum foil and a saturated calomel electrode were placed inside the glass tube. The schematic diagram of the experimental cell assembly is described elsewhere [32]. The assembly was connected to electrochemical impedance analyzer (PARSTAT 2273, EG&G). Impedance measurements were carried out for a frequency range of 100 KHz to 0.01 Hz with an ac amplitude of 20 mV for different immersion time up to 5 days using POWER SINE software. The impedance values are reproducible ±2 to 3%. From the impedance plots, the coating resistance (Rc), the coating capacitance (Cc), the charge transfer resistance (Rct) and the double layer capacitance (Cd) values were calculated using the equivalent circuit shown in Fig. 1. In the equivalent circuit, Rₚ represents the solution resistance, Rₚ represents the coating resistance, CPE 1 represents the constant phase element for coating capacitance, Rₚ represents the charge transfer resistance and CPE 2 represents the constant phase element for double layer capacitance.

For the description of a frequency independent phase shift between an applied AC potential and its current response, a constant phase element (CPE) is used which is defined in impedance representation as

\[
Z(\text{CPE}) = Y_0(\omega)^{-n}
\]

where \(Y_0\) is the CPE constant, \(\omega\) the angular frequency (in rad s⁻¹), \(j^2 = -1\) the imaginary number and \(n\) is the CPE exponent. Depending on \(n\), CPE can represent resistance (\(Z(\text{CPE}) = R, n = 0\)), capacitance (\(Z(\text{CPE}) = C, n = 1\)), inductance (\(Z(\text{CPE}) = L, n = -1\)) or Warburg impedance for \(n = 0.5\) [33]. The following equations have been used to convert \(Y_0\) into coating capacitance \(C_c\) and double layer capacitance \(C_d\) [34] from the impedance values of high and low frequency semicircles, \(C_c\) or \(C_d\) = \(Y_0(\omega_m)^{n-1}\) where \(\omega_m\) is the angular frequency at which \(Z''\) is maximum of the corresponding semicircle.

**3. Results and discussion**

**3.1. FTIR spectral characterization**

Fig. 2(A) shows the FTIR spectra of Fe₂O₃ and PANI. The bands at 1561 and 1474 cm⁻¹ of PANI (curve a) are the stretching mode of C=O and C≡C of quinoid and benzenoid rings. The bands at 1296 and 1242 cm⁻¹ have been attributed to C–N stretching mode of benzenoid ring and band at 1110 cm⁻¹ is due to a plane bending vibration of C–H. The curve b in Fig. 2(A)
indicates the FTIR spectra of Fe_{2}O_{3}, where the bands around 500–400 cm\(^{-1}\) are assigned to Fe–O stretch. The FTIR spectra of PFC are shown in Fig. 2(B). It can be seen that the FTIR spectra of the composites are similar to that of pure PANI while the bands for C=N, C=C and C=N all shifted to lower wave numbers, i.e. 1555, 1444, 1285 and 1233 cm\(^{-1}\) due to strong interaction of Fe_{2}O_{3} and polyaniline. Such type of red shift has been reported for PANI–TiO_{2} [35], PANI–Fe_{3}O_{4} [27], PANI–MnO_{2} [31] and PANI–ZrO_{2} [36] composites.

### 3.2. XRD characterization

Fig. 3(a) shows the X-ray diffraction pattern of PANI. Diffraction pattern of PANI have a broad peak at about 2\(\theta\) = 25.0 which is the characteristic peak of PANI [37,38]. Fig 3(b) shows the XRD pattern of Fe_{2}O_{3} and Fig 3(c) shows the XRD pattern of PFC (1:1). It can be seen that the PFC XRD pattern is very much similar to that of Fe_{2}O_{3} and the broad diffractive peak of PANI has become weak. This indicates that PANI deposited on the surface of Fe_{2}O_{3} has no effect on the crystalline structure of Fe_{2}O_{3}. Besides, these results indicate that PANI is amorphous in the PANI–Fe_{2}O_{3} composite since the molecular chain of the adsorbed PANI is confined and the degree of crystallinity is decreased [39].

### 3.3. Morphology of the composites

Fig. 4(a–e) shows the SEM pictures of Fe_{2}O_{3}, PANI and PFCs. Morphology examinations revealed that at higher ratios of Fe_{2}O_{3}:aniline, the round shaped Fe_{2}O_{3} particles with few PANI adhered are observed due to preferential polymerization of aniline on Fe_{2}O_{3} particles while at lower ratios, Fe_{2}O_{3} particles with thick PANI layer and adsorbed PANI particles are observed due to secondary nucleation effect of primary formed PANI layer. Besides, the colour of the composites was found to be dark brown in the case of higher Fe_{2}O_{3} content while the composite appeared dark green for lower Fe_{2}O_{3} content.
peel off the PANI layers was observed for all samples indicated the good adhesion of the PANI layer on the Fe$_2$O$_3$ particles.

### 3.4. Conductivity characteristics

The conductivity values obtained for the pure PANI and PFC are: PANI: 2.17 S cm$^{-1}$; PFC (1:2): 0.04 S cm$^{-1}$; PFC (1:1): 0.025 S cm$^{-1}$ and PFC (2:1): 0.033 S cm$^{-1}$. It can be seen that the composites have the same order of conductivity. However, these values are two orders less than the conductivity of PANI.

### 3.5. EIS measurements

The corrosion protection performance of the coating containing Fe$_2$O$_3$, Fe$_2$O$_3$ + PANI and PFC have been found by EIS method on the coated panels in 3% NaCl solution. Fig. 5 shows the impedance behaviour of Fe$_2$O$_3$ containing coating and Table 1 gives the impedance parameters derived from these curves. The resistance of the coating is found to be decreased from 74.7 to 5 k$\Omega$ cm$^2$ after 3 days immersion and attained 1.4 k$\Omega$ cm$^2$ after 5 days immersion. The $R_{ct}$ values are also decreased from 45 to 1.5 k$\Omega$ cm$^2$ after 5 days immersion. This indicates the loss of protective property after 3 days of immersion. This observation has been confirmed by the marked increase of $C_{dl}$ values from $1.5 \times 10^{-8}$ to $5.2 \times 10^{-3}$ F cm$^{-2}$.

Fig. 6 shows the impedance behaviour of coating containing Fe$_2$O$_3$ and PANI added separately in 3% NaCl. The impedance parameters obtained from these curves are also given in Table 1. The coating resistance which is 4.91 k$\Omega$ cm$^2$...
Table 1
Impedance parameters of Fe$_2$O$_3$ and Fe$_2$O$_3$ + PANI pigmented coatings on steel in 3% NaCl

<table>
<thead>
<tr>
<th>Time days</th>
<th>Coating resistance $R_c$ ($\Omega$ cm$^2$)</th>
<th>Coating capacitance $C_c$ (F cm$^{-2}$)</th>
<th>Charge transfer resistance $R_{ct}$ ($\Omega$ cm$^2$)</th>
<th>Double layer capacitance $C_{dl}$ (F cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$O$_3$</td>
<td>1</td>
<td>$7.47 \times 10^4$</td>
<td>$3.53 \times 10^{-8}$</td>
<td>$4.54 \times 10^4$</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>$5.00 \times 10^3$</td>
<td>$4.48 \times 10^{-8}$</td>
<td>$2.81 \times 10^3$</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>$1.42 \times 10^3$</td>
<td>$1.70 \times 10^{-7}$</td>
<td>$1.50 \times 10^3$</td>
</tr>
<tr>
<td>Fe$_2$O$_3$ + PANI</td>
<td>1</td>
<td>$4.91 \times 10^3$</td>
<td>$2.23 \times 10^{-9}$</td>
<td>$1.57 \times 10^4$</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>$3.21 \times 10^3$</td>
<td>$2.58 \times 10^{-9}$</td>
<td>$8.66 \times 10^3$</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>$4.12 \times 10^3$</td>
<td>$3.19 \times 10^{-9}$</td>
<td>$8.51 \times 10^3$</td>
</tr>
</tbody>
</table>

Figs. 5–9 show the variation of impedance of coating containing PFC with different ratios. Table 2 compares the variation of impedance values for coatings of different composites with period of immersion. The resistance value of the coating for 1:1 composite is found to increase from 31.4 to 80.8 k$\Omega$ cm$^2$ with time and the $R_{ct}$ values are remained in the range of 26.5–28.4 k$\Omega$ cm$^2$ with time. This indicates that the 1:1 composite is able to protect steel more effectively than the coating containing Fe$_2$O$_3$. 

![Fig. 5. Impedance behaviour of Fe$_2$O$_3$ pigmented coating on steel in 3% NaCl. (-) 1 Day; (□) 3 days; (■) 5 days.](image)

![Fig. 6. Impedance behaviour of Fe$_2$O$_3$ + PANI pigmented coating on steel in 3% NaCl. (–) 1 Day; (□) 3 days; (■) 5 days.](image)

![Fig. 7. Impedance behaviour of PFC (1:1) pigmented coating on steel in 3% NaCl. (–) 1 Day; (□) 3 days; (■) 5 days.](image)

![Fig. 8. Impedance behaviour of PFC (1:2) pigmented coating on steel in 3% NaCl. (–) 1 Day; (□) 3 days; (■) 5 days.](image)
Fe₂O₃. In the case of 2:1 ratio (aniline:Fe₂O₃) even though the composite depends upon the morphology of PANI deposited on PFC (2:1) the values are decreased from 62.1 to 12.1 kΩ cm².

PFC (1:2) is cyclically oxidized to PANI (ES) by the reduction of oxygen in the oxidative region and the PANI (LB) which has been reduced as being responsible for establishing the potential of iron in passive region and the PANI–Fe₂O₃ composite (1:1) is found to offer higher corrosion protection.

The above studies show that the coating containing 1:2 composite, the corrosion resistance is found to be constant in the range of 15.0–14.8 kΩ cm² with time. The charge transfer resistance values are decreased from 62.1 to 12.1 kΩ cm² with time. Even though the coating capacitance values are remained at 3.2 to 3.1 × 10⁻⁹ F cm⁻² with time, the C≡ values are found to be very high, i.e. 1.11 × 10⁻⁵ to 1.5 × 10⁻³ F cm².

For the coating containing 2:1 composite there is a marked decrease of both coating resistance and charge transfer resistance values with time which indicates the poor protective property of the coating.

The above studies show that the coating containing PFC formed in 1:1 ratio is found to offer high corrosion protection than that of coating containing Fe₂O₃ and PFCs with 2:1 and 1:2 ratios. The corrosion protection ability of the PANI–Fe₂O₃ composite depends upon the morphology of PANI deposited on Fe₂O₃. In the case of 2:1 ratio (aniline:Fe₂O₃) even though the concentration of PANI deposit is more but the PANI deposits are granular due to secondary nucleation of PANI growth on the already existing PANI [40]. Similar observation has been reported in the case of preparation of PANI–SiO₂ composite [41] and PANI–zinc ferrite composite [42]. But in the case of 1:1 ratio, uniform, thin and adherent PANI coating is formed on Fe₂O₃. However, for 1:2 ratio, the Fe₂O₃ is not fully covered with polyaniline. Hence, the coating containing the PANI–Fe₂O₃ composite (1:1) is found to offer higher corrosion protection.

The better performance of the coating containing 1:1 composite may be due to uniform coverage of Fe₂O₃ by polyaniline polymer. It has been established in earlier studies [5,16,21] that the polyaniline containing coating is able to protect steel by passivation of iron substrate. From SEM and XPS studies, it has been reported that the oxide layer formed in PANI containing coating is mainly of Fe₂O₃ above a very thin Fe₃O₄ layer [16].

The corrosion protection of steel by PANI (ES) containing coating has been ascribed for substrate ennoblement, the formation of a passive oxide film and anodic inhibition through the precipitation of an insoluble metal salt and dopant anion [43]. The PANI (ES) and PANI (LB) redox couple has been regarded as being responsible for establishing the potential of iron in passive region [44,45] and the PANI (LB) which has been reduced is cyclically oxidized to PANI (ES) by the reduction of oxygen so that the potential of iron is maintained always in the noble values [46,47].

The oxide film is reported to be γ-Fe₂O₃ [16] along with iron–dopant salt film [9]. Hence, the higher corrosion protection offered by PANI–Fe₂O₃ composite with phosphate dopant containing coating may be due to the formation of passive film along with iron–phosphate salt film on the iron surface. But in the case of bare Fe₂O₃ containing coating, the corrosion protection is mainly due to the barrier effect which offers less amount of corrosion protection in comparison to that of PANI–Fe₂O₃ composite containing coating.

4. Conclusions

The polyaniline–Fe₂O₃ composite has been prepared by chemical oxidative method in the presence of aniline and Fe₂O₃ by ammonium persulphate oxidant in phosphoric acid medium.
The XRD pattern shows that the polyaniline has no effect on the crystalline behaviour of Fe₂O₃. The corrosion resistant property of the coating containing 1:1 composite is found to be higher than that of Fe₂O₃ and other 1:2 and 2:1 polyaniline–Fe₂O₃ composites.

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References