



# Synthesis of polyaniline/montmorillonite nanocomposites with an enhanced anticorrosive performance



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## ABSTRACT

Polyaniline/montmorillonite (PANI/Mt) nanocomposites (1–7% (w/w) Mt based on the aniline content) were synthesized by *in situ* chemical oxidative polymerization with a 73.4–75.8% monomer conversion level. Fourier-transform infrared and scanning electron microscopy analyses confirmed the presence of Mt incorporation into PANI, whilst X-ray diffraction analysis revealed the exfoliated structure and that PANI was intercalated between the Mt layers. Thermogravimetric analysis revealed that the thermal properties of PANI and PANI/Mt composites were enhanced with increasing Mt levels.

The corrosion protection of steel coated with PANI/Mt nanocomposites was investigated using cyclic voltammetry, and revealed that PANI/Mt nanocomposites showed an enhanced corrosion protection of steel against 1.0 M H<sub>2</sub>SO<sub>4</sub> in comparison to that of a pure PANI coating. Increasing the Mt content in the PANI/Mt nanocomposites and the applied film thickness (10–50 μm) both improved the anticorrosive properties, presumably due to an increasing tortuosity of the diffusion pathway for corrosion agents. The best corrosion resistance of steel to salt spray was, however, obtained with a PANI/Mt nanocomposite with 5% (w/w) Mt when applied as a 50 μm thick film.

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## 1. Introduction

Polyaniline (PANI) is one of the widely studied organic conducting polymers because of its high conductivity, excellent environmental stability and optical properties, its ease of preparation (its limited solubility) and relatively low cost and its protective properties against environmental corrosion [1–6]. Indeed, one of the important applications of PANI is as an anticorrosive coating on metal, where it has been shown to be able to protect steel in alkali, neutral and acidic environments [7–11]. PANI is a good candidate as an anticorrosive coating to replace chromium-containing coatings, which have adverse health and environmental concerns [12]. PANI has both barrier and electrochemical protection effects that cause an increase in the corrosion potential and forms a protective, passive iron-dopant oxide anodized layer (mainly Fe<sub>2</sub>O<sub>3</sub> above a thin Fe<sub>3</sub>O<sub>4</sub> layer) on the metal surface due to its redox catalytic properties, which is then able to protect the small defects and pinholes in the coatings [13–18]. However, PANI coatings are limited by their mechanical strength, adhesion to the steel and the effectiveness of their barrier effect and so the synthesis of PANI

composites is required and of interest to remedy these limitations of PANI coatings and so increases its efficiency in corrosion protection. The pretreatment of the metal surface by chelating agents [19], pre-deposition of the polymers [20] and formation of a passive stable layer on the metal surface can all increase the adhesion of PANI [21–23].

The formation of PANI composites with inorganic materials including layered silicates (nanoclays) is one strategy currently being evaluated to increase the effectiveness of PANI as anticorrosive coating on metals [24–26]. The ultrafine particle size, large surface area and intercalation properties with their unique structure and reactivity together with their high strength, stiffness, aspect ratio and ability to allow intercalation of other polymers all make nanoclays highly suitable as fillers. Montmorillonite (Mt) is a layered smectite silicate based clay material that has attracted much interest in the preparation of polymer/clay nanocomposites (PCN). PCNs have been found to have an enhanced gas barrier, thermal stability, mechanical strength, fire retardant and anticorrosive properties [27–29]. Mt can enhance the anticorrosive properties of PANI coatings due to its improvement of the barrier property of PANI [30,31].

Recently, increasing research attention has been paid to PCNs, and especially to PANI/Mt nanocomposites, for corrosion protection. There are three broad types of PCN (phase separated microcomposites, intercalated nanocomposites and exfoliated

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nanocomposites), depending on the interfacial interaction strength of the polymer matrix and the silicate layer. The exfoliated PANI/Mt nanocomposites prepared by *in situ* polymerization showed an exfoliation of the clay layers in the polymer matrix at the nanoscale, as determined from the X-ray diffraction (XRD) patterns [32]. With respect to the mechanical properties, PANI/organophilic Mt (O-Mt) nanocomposites exhibited improved tensile properties, including the Young's modulus, fracture toughness, hardness and impact energy, with the presence of Mt up to 23% (w/w) [33]. For corrosion protection, iron coated with a PANI/Mt nanocomposite with 5% (w/w) Mt comprised of both hydrophilic (e.g. Na-Mt) and O-Mt nanoclay particles showed a better anticorrosive property than that with a pure PANI coating or with either PANI/Na-Mt or PANI/O-Mt [27]. Nanocomposites of PANI with natural clinoptilolite (Clino) were successfully synthesized by *in situ* polymerization and the PANI/Clino nanocomposite with 3% (w/w) clino showed a much lower corrosion current of coated iron samples than the pure PANI coated samples or those coated with PANI/Clino nanocomposites at a 1 or 5% (w/w) clino content [8].

In this work, PANI/Mt nanocomposites comprised of Mt with organophilic characteristics were synthesized by *in situ* chemical oxidative polymerization. The effects of varying the Mt loading level and the applied film thickness on the anticorrosive properties of the PANI/Mt nanocomposite coatings were investigated and compared to those for the pure PANI coating.

## 2. Experimental

### 2.1. Materials

Aniline (Loba Chemie), ammonium persulphate (APS, Ajax Finechem), hydrochloric acid (37% HCl, QR c), ammonia solution (25% NH<sub>4</sub>OH, QR c), methanol (QR c) and N-methylpyrrolidone (NMP, QR c) were used as received. Cloisite15A (CS15A), a natural O-Mt modified with 30% (w/w) of quaternary ammonium salt with cation exchange capacity of 125 meq/100 g clay to provide hydrophilic properties, was supplied by Southern Clay Products.

### 2.2. Synthesis of PANI and PANI/Mt nanocomposites

PANI (4 g) was prepared by *in situ* chemical oxidation polymerization of aniline and was performed in 1 M HCl solution (200 mL) using 0.177 M APS as an oxidant/initiator. The reaction mixture was vigorously stirred at 0–5 °C for 6 h. The precipitated emeraldine salt was obtained by filtration, washed with excess 4:1 (v/v) distilled water: methanol and dried in a vacuum oven at 50 °C for 48 h. The emeraldine salt form of PANI (3.0–3.4 g) was then dedoped with 500 mL 1 M ammonia solution for 4 h followed by washing and drying as above to leave the emeraldine base as a dark brown powder. Then, 1 g of this emeraldine base form of PANI was dissolved in 40 mL of NMP with stirring at room temperature for 7 h. The resulting viscous solution was filtered to remove any insoluble particles. The PANI/Mt nanocomposites were prepared by similar procedure except the Mt was added to the aniline prior to polymerization. The effect of the Mt loading level were studied over the range of 1–7% (w/w based on aniline content) Mt.

The monomer conversion level was determined by gravimetric calculation as in Eq. (1):

$$\text{monomer conversion (\%)} = \frac{M_0 - M_1}{M_2} \times 100, \quad (1)$$

where  $M_0$ ,  $M_1$  and  $M_2$  are the mass of the prepared composite particles, charged Mt particles, and charged aniline monomer, respectively.

### 2.3. Coating of PANI/Mt nanocomposites on steel samples

Steel spring sheet (SK5) coupons of 1 cm × 1 cm × 0.1 cm (for Tafel slope study) and 2 cm × 5 cm × 0.1 cm (for salt spray test) were used in the corrosion studies. In order to remove any existing passive film, the steel coupons were mechanically polished using 150 and 400 grade emery papers followed by rinsing with distilled water and acetone prior to coating with PANI or the respective PANI/Mt nanocomposites. The respective PANI or PANI/Mt coating polymer solvated in NMP (Section 2.2) was deposited by high-pressure air spraying and then the solvent was evaporated in a vacuum oven at 40 °C for 24 h to leave a dry film. Film of different thickness (10, 20, 30, 40 and 50 μm) on the steel spring sheets were obtained by repeated spraying for several times, and the thickness of films was measured using an electronic outside micrometer. The measurement was taken from three different points distributed over the sample, and the values averaged. The prepared samples were then evaluated for their corrosion resistance (Section 2.6) and film morphology (Section 2.5).

### 2.4. Characterization of PANI/Mt nanocomposites

Fourier transform infrared (FT-IR) spectra were recorded over the 4000–400 cm<sup>-1</sup> range using a Spectrum GX Perkin Elmer with the sample pressed into a KBr disk. XRD patterns were recorded using a Bruker AXS Model D8 Discover with Cu Kα radiation at 40 kV and 40 mA with a 2θ range from 1° to 35°, step time of 0.3 s and step size of 0.02°. Thermogravimetric analysis (TGA) was performed using a Perkin Elmer, Pyris diamond model. The samples were heated from room temperature to 700 °C at a heating rate of 10 °C/min under a 50 mL/min nitrogen flow rate.

### 2.5. Morphological study

The morphology of the nanocomposites was investigated by scanning electron microscopy (SEM) using a JEOL Model JSM-5410 LV microscope. For the cross-sectional morphology of PANI/Mt nanocomposites, a dried steel sample was placed in a PVC ring form and fully immersed in acrylic and phenolic resins with a curing time of 7 min at 180 °C and 30 kPa. The resin-covered sample was sectioned, polished, washed by ethanol and dried prior to examination.

### 2.6. Corrosion study

The anticorrosive performance of the PANI/Mt nanocomposite-coated steel samples was evaluated from their electrochemical Tafel slope using a conventional three-electrode. The coated samples were recorded by sweeping the potential from the equilibrium potential toward the negative and positive potentials against a Ag/AgCl reference electrode in 1 M H<sub>2</sub>SO<sub>4</sub> electrolyte.

The corrosion resistance of coated steel samples was also measured according to the standard ASTM B117 testing method using a salt spray tester. Samples were immersed under a 5% (w/v) NaCl solution environment and examined for the appearance of corrosion every 12 h over a time period of 97 h.

## 3. Results and discussion

### 3.1. Effect of the Mt loading level on the synthesis of PANI/Mt nanocomposites

The effect of the Mt loading level on the aniline monomer conversion level to PANI was studied over the range of 1–7% (w/w, based on the aniline weight), and the results are summarized in Table 1. The aniline conversion level slightly decreased (1.04– to 1.07-fold at 1–7% (w/w) Mt, respectively) with an increasing

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