



# Convenient routes to synthesize uncommon vaterite nanoparticles and the nanocomposites of alkyd resin/polyaniline/vaterite: The latter possessing superior anticorrosive performance on mild steel surfaces



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## ARTICLE INFO

### Article history:

Received 9 September 2013

Received in revised form

17 November 2013

Accepted 25 November 2013

Available online 11 December 2013

### Keywords:

Polyaniline

Anticorrosive surface coatings

Natural calcite

Vaterite

corrosion resistance

## ABSTRACT

Polyaniline (PANI)/Precipitated Calcium Carbonate (PCC) composite materials are prepared, for the first time, starting from naturally occurring calcite, and are well characterized. X-ray diffraction (XRD) studies provide information for the presence of unstable vaterite form of PCC in the composites, with an average crystallite size of 26 nm, thus demonstrating the ability of PANI to stabilize, otherwise unstable, vaterite phase of  $\text{CaCO}_3$ . Thermal analytical results (TGA and DSC) also provide information for the presence of only PANI and PCC, thus providing information for the purity of the composites. This method, therefore, provides a convenient route to prepare vaterite nanoparticles. Electron Microscopic (FE-SEM) images of the composites confirm that the voids of PANI chains are filled by the spherical nanoparticles of vaterite of diameter  $\sim 24$  nm, to result in spheres of the composites with an average diameter of 3–4  $\mu\text{m}$ . FTIR spectra show that the PANI exists in its emeraldine form, weakly protonated when prepared at pH 5. Analysis of the FT-IR data for the four composites of PANI/vaterite gives the molar ratios of PANI:vaterite to be 1:4, 1:2, 1:1, 2:1, respectively. The PANI/PCC composites show electrical conductivity of  $\sim 1.00 \times 10^{-5}$  S  $\text{cm}^{-1}$ , which is an impressive value to use these materials as anticorrosive coatings. AC impedance studies also give the conductivities of the PANI/PCC composites to be corresponding to a weakly electronically-conductive emeraldine form of PANI, with equal contributions from the ionic and electronic components, irrespective of the different amounts of vaterite or calcite present in the composites. The DC polarization test confirms equal transport numbers for ions and electrons in PANI samples. The above composites of PANI/vaterite, and a composite of 1:1 molar ratio of PANI/calcite, were mixed with alkyd resin and xylene, separately, to prepare anticorrosive coatings on mild steel (Mole percentages: 98.90% Fe, 0.26% C, 0.04% P, 0.05% S and 0.75% Mn) surfaces. All five composite coatings, with thickness  $\sim 40$   $\mu\text{m}$ , show dramatic decrease in corrosion current density, and a considerable increase in corrosion resistance, to result in several orders of magnitude lowering of the corrosion rate from that of bare mild steel surfaces and those coated with only alkyd resin. There are considerable positive shifts in the corrosion potential also, when each of the five coatings are applied, separately, on mild steel samples, which provide information for a significant overpotentials induced by these coatings on iron oxidation. All four Alkyd resin/PANI/vaterite coatings show higher anticorrosive performances (by factors of  $2 \times 10^4$ ,  $5 \times 10^4$ ,  $1 \times 10^5$  and  $1.67 \times 10^4$ , respectively from that of bare mild steel) than that of the Alkyd resin/PANI/calcite coating (by a factor of  $1.25 \times 10^3$  from the same). The improved pore-sealing by relatively smaller (26 nm diameter) and spherical vaterite nanoparticles, when compared with a little larger (38 nm) and somewhat elongated nanoparticles of calcite, is suggested to be responsible for better anticorrosive performance of the Alkyd resin/PANI/vaterite nanocomposites.

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## 1. Introduction

Polyaniline (PANI) has gained a great deal of attraction, in recent years, as anticorrosive protective coatings on surfaces of metals and metal alloys [1–7]. PANI is one of the most extensively used

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conductive polymers, for application as anticorrosive coatings, and for numerous other technological applications, due to its environmental stability, variable electrical conductivity, electrochromic properties, readily availability of the cheap monomer aniline, and its low production cost [8–10]. Usually, PANI-based anticorrosive paints are prepared by including PANI to alkyd or epoxy resins [4,5,11,12]. These paints have an ability to protect metals and alloys, which are susceptible for corrosion [13]. Other than preparation of anticorrosive coatings, PANI has applications in the replacement of expensive metals in electronic products, plastic batteries, piezoelectric devices and so on. [11,14,15]. However, some drawbacks are also associated with PANI, which include poor adhesion, low abrasion resistance and poor thermal stability, which hamper its use as coatings [9]. These problems, associated with PANI, can be overcome, to some extent, by incorporating fillers such as Precipitated Calcium Carbonate (PCC) to result in PANI/PCC composite materials, which have synergistic properties of both the polymer and the PCC product [11,16,17]. However, to the best of our knowledge, there are only a very limited number of reported studies on the synthesis of PANI/PCC composites and their coatings [9,11,17,18].

The use of conducting polymers, in general, and polyaniline, in particular, as an additive in anticorrosive paints applied on steel structures of ships and various other steel structures, including various forms of steel, such as stainless steel, mild steel and carbon steel, is well known, and a vast literature is available to this effect [1–3,5,6,12,13]. Possible mechanisms for the anticorrosive properties of polyaniline coatings have also been well documented [1,2,19–21]. Many researchers ascribe the corrosion protection by polyaniline containing coatings to be due to protective barrier effect by the paint [1–3,5,6,12,13], but some others postulate that the protection from corrosion, by polyaniline, is due to the anodic protection through the redox chemistry of polyaniline, where the iron surface is oxidized to iron hydroxide while the emeraldine salt form of polyaniline is reduced to its' leucoemeraldine salt form [22]. The emeraldine salt form is then regenerated by the atmospheric oxygen. However, due to the barrier effect to the restriction of the penetration of oxygen through the polymer, and the passivation layer of  $\text{Fe}(\text{OH})_3$  produced on the iron surface, the further oxidation of iron is prevented. [19]. There are some references which deal with cathodic protection of iron and steel by polyaniline [20,21]. From the fundamental electrochemical point of view, all these mechanisms are possible for the prevention of corrosion of iron and steel objects from polyaniline. As regards to the barrier effect, neat polyaniline structure contains ample voids for adequate penetration of oxygen gas towards the iron surface. The advantage of the nanocomposites of polyaniline and nanoscale inorganic fillers is that the filler particles are set in the void spaces of the polymer, and are stabilized by favorable interactions of the surface groups or ions on the surfaces of the filler particles and the polar groups of polyaniline. This makes the composite material to be virtually pin-hole free for the prevention of the penetration of oxygen molecules to reach the iron surface. Additionally, the rich redox chemistry of polyaniline, particularly, when it is present in relatively lesser-conducting emeraldine salt form, as is the case with our nanocomposites of PANI/PCC, can make sure the anodic protection from corrosion also. However, if highly conducting emeraldine salt form of polyaniline is used, a considerable extent of corrosion can take place through the oxidation of iron and reduction of the emeraldine salt form of polyaniline. As such, from both electrochemical and barrier point of views, the PANI/PCC nanocomposites, which we have prepared, have the advantage of protecting the iron objects from corrosion through both mechanisms.

PCC is a material with high demand, good quality and inexpensive filler in industries, such as paper, textile, rubber, plastic, paint, cosmetic, sealant, tooth paste and in the food industry [23–25].

The applications of PCC products depend on their morphology and polymorphism, which are usually controlled by organic additives such as polymers used in their synthesis [26,27]. Hence, most of researchers attempt to synthesize PCCs with various morphologies and phases [28–30]. PCC occurs in amorphous phase, as well as in three crystalline phases of stable calcite (over 90% natural abundance out of the three forms), moderately stable aragonite and unstable vaterite (very rare) forms [31]. Furthermore, stabilization of unstable vaterite phase has become a great effort in recent years [30–33] since vaterite is essential to prepare bone implant materials, nanotube-coated, biocompatible composites and to replace silica in the coating pigments [32–38].

In this paper, we report a novel method to synthesize PANI/PCC composite, using naturally occurring calcite, to use them as anticorrosive protective-coatings on mild steel surfaces. The PCC produced by this method is present in its vaterite form. The synthesis of vaterite form of PCC is very difficult owing to its thermodynamic instability even in the aqueous solution at ambient conditions, but this method has provided us of a convenient route to, otherwise difficult to prepare, vaterite form of the PCC. In the preparation of PANI/PCC, aniline is polymerized *in situ* by persulfate ions in a calcium chloride solution, the latter was prepared by reacting naturally occurring calcite with hydrochloric acid. Subsequent to polymerization, sodium carbonate is added to the mixture to form PCC. The anticorrosive paint is prepared by adding the composite to a mixture of xylene and alkyd resin to coat on mild steel surfaces. This approach is very important for the development of natural calcite-based products in surface coating industries. On the other hand, use of calcite as calcium source is an attractive choice, since calcite is one of the most extensively available minerals in the world. The synthesized PANI/PCC composite coatings show a reasonable conductivity and very high corrosion resistance compared to Alkyd resin/PANI coatings or just Alkyd resin coatings on mild steel. Furthermore, this method provides a convenient route to prepare vaterite nanoparticles, since PANI stabilizes the vaterite form of PCC, and also PANI prevents the aggregation of these nanoparticles.

## 2. Experimental

### 2.1. 2.1 Materials

Aniline (99.5% purity), sodium persulfate (99.9% purity), hydrochloric acid (36.5% assay) and sodium carbonate (99.9% purity) used were of analytical grade and were purchased from Sigma-Aldrich. Commercial grade alkyd resin, xylene and mild steel (with the mol% of 98.90% Fe, 0.26% C, 0.04% P, 0.05% S and 0.75% Mn; according to the manufacturer's specifications) were purchased from the Sri Lankan market. Aniline used was freshly distilled. Calcite samples were collected from a marble quarry at Balangoda, Sri Lanka and were characterized as explained in Section 3.1.

### 2.2. Preparation of PANI/vaterite composite material

Calcite samples were crushed, ground and the powdered fraction of particle sizes less than  $150\ \mu\text{m}$  was digested in 1.0 M HCl solution, to obtain 100.0 mL of 1.0 M  $\text{CaCl}_2$  solution, at pH 2, to use as calcium source of the PCC products. The  $\text{CaCl}_2$  solution was placed in a two-neck, round-bottom flask and 2.3 mL of freshly distilled aniline was added and mixed well, while maintaining the solution at pH 2, by using HCl to adjust the pH. Sodium persulfate aqueous solution (0.5 M, 100.0 mL) was then added dropwise to this mixture, while stirring, to initiate the polymerization of aniline. After the green PANI particles were appeared, 1.0 M  $\text{Na}_2\text{CO}_3$  solution was added dropwise, until the pH of the medium reaches 5, in order

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