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Methodology for zinc phosphate pigment incorporation into polypyrrole matrix

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Abstract

In this work, the incorporation of a commercial zinc phosphate pigment into polypyrrole (PPy) matrix during its electrochemical synthesis on mild steel was studied in order to produce PPy/zinc phosphate composite films as a protective layer against corrosion. Potassium nitrate, oxalic acid, tosylic acid and sodium salicylate solutions were used as electrolytes in cyclic voltammetry and galvanostatic polarisation studies. The influence of synthesis parameters such as nature, concentration, pH and stirring of the electrolyte on the degree of incorporation of the pigment was investigated, as well as time and current densities of the electropolymerisation process. Their influence on current efficiency was also evaluated. Sodium salicylate was the only electrolyte to show a high current efficiency in the polymerisation reaction and to yield a composite film with a reasonable amount of zinc phosphate. In this electrolyte medium, X-ray photoelectron spectroscopy (XPS) analysis showed that zinc phosphate may be found in the polymeric matrix: (i) as a conductive ionic minority form and (ii) as a non-conductive non-ionic majority one for higher incorporation levels. Scanning electron microscopy (SEM) showed that zinc phosphate is heterogeneously distributed on the surface of the polymer.

1. Introduction

The corrosion inhibition on steel surfaces attributed to electrically conductive polymers (ECP), like polypyrrole (PPy), is partly due to the formation of passivating stable oxide films such as Fe_3O_4, α-Fe_2O_3 and γ-Fe_2O_3 at the metal surface [1]. Pigments can be incorporated into the PPy matrix in order to improve this protection. Pigments may protect metal by physicochemical (barrier mechanism), electrochemical or ion exchange mechanisms [2].

The incorporation of minerals such as TiO_2, SiO_2, MnO_2 and WO_3 into PPy matrix in order to change or improve polymer properties has been reported [3–9]. As PPy is insoluble and infusible, *in situ* incorporation during its anodic electrosynthesis is the most usual method. There are few studies devoted to the incorporation mechanisms of solid particles into PPy. It was supposed [7] that solid particles impinge onto the substrate on which PPy is being electrodeposited. Their incorporation is governed by the surface concentration of defects in the PPy matrix. Particles with a minimum kinetic energy are capable of being attached to PPy after colliding with its surface. As PPy grows as micro-hemispheres, the solid particles are incorporated into PPy concavities, in the valleys or summits.

The authors' previous work has shown that TiO_2 incorporation into a PPy matrix during its electrochemical synthesis on mild steel leads to PPy/TiO_2 composite films containing up to 6.5 weight % of TiO_2 [8]. However, when the electrolyte is stirred with a pump in a loop system, the incorporation of the pigment rises to 14 weight % in the PPy matrix [9]. These composites showed a 50% reduction in the corrosion rate of mild steel.

In this work, a commercial zinc phosphate pigment was incorporated into a PPy matrix. This is a well-known pigment that displays anticorrosion properties. Moreover, this pigment is considered as environmentally acceptable, being an alternative to chromium based pigments [2]. Zinc phosphate pigment can improve anticorrosion properties of PPy through passivating and barrier mechanisms. It possibly repairs defects in the iron oxide layer formed by ECP action on mild steel that was extensively exposed to an aggressive medium. This is a kind of passivation. For barrier action, zinc phosphate contributes with its own morphology since the water permeability of coatings decreases significantly if plate- or flake-shaped pigments, like zinc phosphate, are used instead of globular-shaped pigments [10].

The evaluation of the protective action of PPy/zinc phosphate composite films on mild steel has already been studied [11]. The PPy/zinc phosphate composite film showed an improvement in the corrosion protection of mild steel with respect to PPy films. However, the zinc phosphate pigment incorporation into the PPy matrix is not a simple process. The influence of some parameters such as nature, concentration, pH and stirring of the electrolyte on zinc phosphate incorporation into PPy was the aim of this study.

2. Experimental

2.1. *Electrochemical synthesis*

The electrolytes used with 0.5 M pyrrole monomer (Aldrich) were: 0.1 M oxalic acid, 0.1 M potassium nitrate, 0.1 M tosylic acid and 1 M sodium salicylate. The average particle size of the zinc phosphate pigment (Hans Heubach) was 2.5 μm and its water solubility is 0.01 weight %. Its composition is zinc (55–57 weight %), phosphorus as phosphate (38–41 weight %), molybdate as MoO_3 (1.5 weight %) and other inorganic contents that do not exceed 0.9 weight % [12]. $100 \times 20 \times 1$ mm AISI 1010 steel sheets were used as working electrodes. They were degreased with an industrial alkaline degreasing solution (DUROCLEAN 107) followed by treatment with a HNO_3 solution, as described elsewhere [13]. A rectangular $110 \times 85 \times 50$ mm acrylic cell was used for the experiments without electrolyte stirring containing two stainless steel plates as counter-electrodes. A saturated calomel electrode (SCE) was used as reference. This cell was also used for cyclic voltammetry carried out with magnetic stirring and using substrates with 1.5 cm^2 exposed area.

For experiments with strong electrolyte stirring, a system with looping similar to that described previously [7, 9] was employed. In this system, a stationary sheet anode was fixed between two stainless steel counter-electrodes and the suspension circulated in a loop with the aid of a pump (PSM suction pump), which produced flow rates from 1 to 15 ml s^{-1}. An Ag/AgCl wire was used as secondary reference electrode. Electrochemical polymer synthesis was galvanostatically performed with an exposed area of 24 cm^2.

2.2. *Zinc phosphate concentration and distribution within the PPy/zinc phosphate composite film*

The PPy/zinc phosphate composite films were degraded in hot concentrated sulphuric acid. The metals were quantitatively analysed by Atomic Absorption Spectroscopy with a GBC 902 Double Beam spectrophotometer (wavelengths of 213.9 nm for zinc and 248.3 nm for iron analyses). Phosphorous was determined as phosphate by the photometrical technique called the Molybdenum Blue Method (P 14848-Merck) with a Skalar 6000 photometer at 712 nm.

A SSI ×100 photoelectron spectrometer with an aluminium monochromatic source (Al Kα radiation 1486.6 eV) was used for X-Ray Photoelectron Spectroscopy (XPS) experiments. These analyses were carried out using a spot size of 600 μm and a vacuum of 10^{-9} Torr (1.33×10^{-7} Pa). An analysis angle of approximately 90° with respect to the sample surface was used. Ar^+ ion bombardment was applied to remove thin layers of the composite films using an AG2 ion gun (Vacuum Generators). The conditions of bombardment were: an acceleration tension of 4.8 kV, an Ar^+ pressure of 5×10^{-6} mbar and 200 μA of ion current. The sputtering rate was approximately 2.5 μm per hour.

The composite film thicknesses were measured using a FISCHER model DUALSCOPE® MP 20 coating thickness meter. SEM experiments were performed using a PHILIPS XL20 scanning electronic microscope. The original zinc phosphate average particle diameter was reduced in order to improve the zinc phosphate incorporation into PPy matrix. They were ground in an agate mortar with an automatic pestle for 5 h. Their size was controlled using a JSM 6100 scanning electron microscope and a Sieve TM 1.3 particle size analyser.

3. Results and discussion

3.1. *Polymerisation parameters definition*

The electrodeposition of conducting polymers onto oxidizable metals is not easy since thermodynamic data predict that the metal will dissolve before the electropolymerisation potential of the monomer is reached. Thus, to achieve the deposition of a conducting polymer on mild steel, it is necessary to find electrochemical conditions that lead to a partial passivation of the metal and decrease its dissolution rate. Also, if a pigment is being codeposited, it must not prevent pyrrole polymerisation.

3.1.1. *Cyclic voltammetry (CV) studies*

These experiments were carried out under magnetic stirring using 0.5 M pyrrole with and without the addition of 20 g l^{-1} zinc phosphate. The exposed electrode area was 1.5 cm^2. The potential was swept from −1 V to 1 V and returning to −1 V (versus SCE). The sweep rate was 50 mV s^{-1}.

3.1.1.1. 0.1 M Potassium nitrate. In this medium (pH around 7), iron is passivated and pyrrole electropolymerisation is possible even without surface treatment [13, 14]. The cyclic voltammograms obtained in the presence of the zinc phosphate pigment, Figure 1, are similar to those without pigment addition [8]. In the first sweep, there is a peak assigned to pyrrole oxidation near to 1 V. In the next sweeps, dimers and oligomers present in the electrolyte change the shape of that peak.

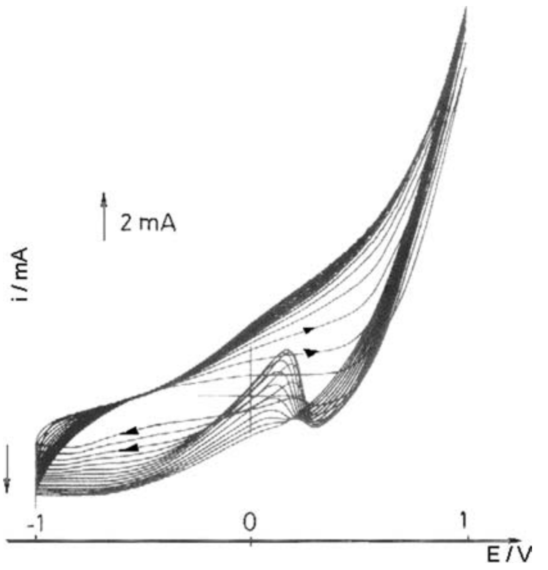

Fig. 1. Cyclic voltammogram of PPy/zinc phosphate composite film synthesis. Electrolyte: 0.1 M KNO_3, 0.5 M pyrrole and 20 g l^{-1} zinc phosphate. 1.5 cm^2 exposed area substrate.

3.1.1.2. 1 M Oxalic acid. A marked difference was observed in the cyclic voltammograms due to the presence of zinc phosphate pigment. Without pigment addition, at pH 6, there is pyrrole polymerisation and at pH 2 there is pyrrole polymerisation only after an induction time. During this time only iron dissolution and passive layer formation on metal surface occur [7]. However, with 20 g l^{-1} zinc phosphate pigment addition, pyrrole polymerisation does not take place at pH 6. At pH 2 (Figure 2), there is only a small current rise with increasing potential indicating little iron corrosion until the third sweep. After that, pyrrole polymerisation takes place.

3.1.1.3. 1 M Tosylic acid (p-toluene sulphonic acid). With or without the pigment, the cyclic voltammograms were similar in this medium. In the voltammograms carried out with addition of 20 g l^{-1} of pigment (Figure 3), an iron oxidation peak beginning before 0 V during the first sweep was observed. After that, the current density of the iron oxidation peak decreased. Pyrrole oxidation was also observed.

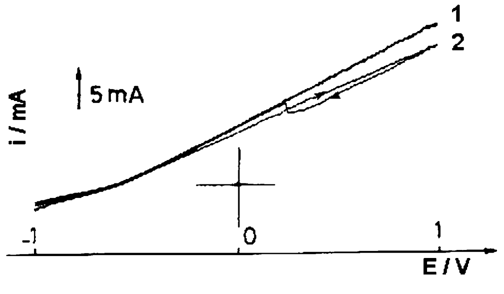

Fig. 2. Cyclic voltammogram of PPy/zinc phosphate composite film synthesis – two first sweeps. Electrolytic medium: 0.1 M $H_2C_2O_4$, pH 2, 0.5 M pyrrole and 20 g l^{-1} zinc phosphate. 1.5 cm^2 exposed area substrate.

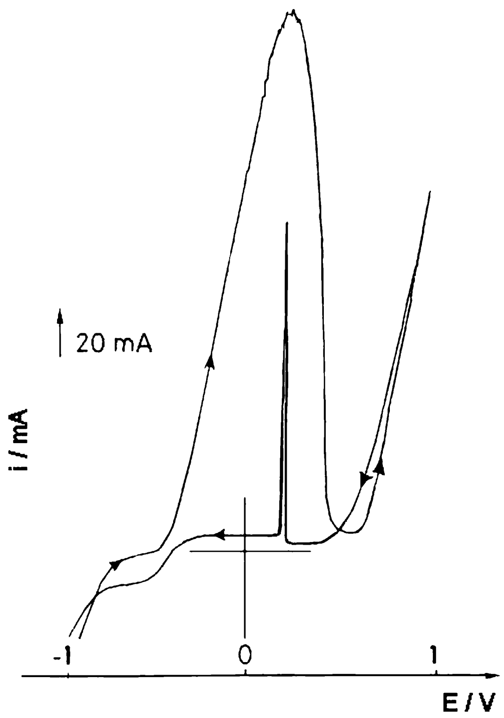

Fig. 3. First cyclic voltammogram of PPy/zinc phosphate composite film synthesis. Electrolytic medium: 1 M tosylic acid, 0.5 M pyrrole and 20 g l^{-1} zinc phosphate. 1.5 cm^2 of exposed area substrate.

3.1.1.4. 1 M Sodium salicylate. Salicylate ions form complex with Zn ions, which precipitates on the electrode and passivate its surface [15]. At low pH values (less than 5) the complex is unstable, so steel corrosion competes with pyrrole polymerisation and the current efficiency for PPy formation is low. The cyclic voltammograms in this medium with or without zinc phosphate pigment are similar and no iron oxidation occurs. Figure 4 shows the cyclic voltammogram of PPy/zinc phosphate composite film synthesis.

As observed by CV experiments, phosphate ions can interfere in pyrrole polymerisation. This fact depends on many factors: the nature and pH of the electrolyte medium, the solubility of the pigment in the medium and others. Phosphate ions, for instance, are more soluble in acid medium. These ions are more soluble in tosylic acid medium (pH 0), 1760 ppm, than in oxalic acid medium (pH 2), only 200 ppm.

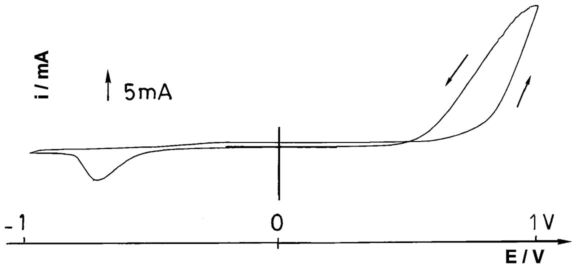

Fig. 4. First cyclic voltammogram of PPy/zinc phosphate composite film synthesis. Electrolytic medium: 1 M sodium salicylate, 0.5 M pyrrole and 20 g l^{-1} zinc phosphate. 1.5 cm^2 exposed area substrate.

As there are many factors involved in pyrrole polymerisation in the presence of zinc phosphate pigment, the determination of phosphate ion performance in the different electrolytes proposed is complex. Also, different polymerisation conditions (applied current density and polymerisation time) for each electrolyte medium were used. Some authors have already evaluated phosphate-containing electrolytes in pyrrole polymerisation [14]. In spite of the fact that phosphate ions promote the passivation of iron – making possible pyrrole polymerisation – all their attempts to obtain PPy using phosphate ions in the electrolyte failed. Thus, it is likely that the phosphate ions passivate the steel and hinder the pyrrole polymerisation in some cases. The best choice of electrolyte is one that promotes PPy formation with high current efficiency and incorporates enough zinc phosphate pigment into the PPy matrix.

3.1.2. *Composite films by galvanostatic polymerisation*

As observed in experiments carried out with TiO_2 as pigment [7–9], a strong convection with a 15 ml s^{-1} flow rate leads to better pigment incorporation and does not decrease the current efficiency of PPy synthesis.

For all electrolytes, Zn and P (in PO_4 form) quantitative analyses did not show a standard deviation of more than 5%. Also, current efficiencies values did not vary by more than 7%.

For polymerisations carried out in KNO_3 medium, current densities of 5 and 10 mA cm^{-2} and 20 min as polymerisation time were the optimum conditions [8, 9]. In oxalic acid medium (pH 2), experiments were performed applying 5 mA cm^{-2} for 30 min. Table 1 shows that there was low zinc phosphate pigment incorporation into the PPy matrix using these media. The increase in zinc phosphate and pyrrole concentration did not significantly increase the incorporation of zinc phosphate pigment into PPy.

Using KNO_3 medium, the current efficiency of PPy formation is the same as without zinc phosphate, around 90%. However, in 0.1 M oxalic acid (pH 2) it was not possible to form a continuous PPy film by galvanostatic polymerisation, probably due to the presence of phosphate ions in the solution. The current efficiency was low, 30%. This confirms the observations made from CV experiments in this medium. Also, only small parts of the electrode were coated with PPy.

In tosylic acid medium, the use of high current densities for short polymerisation time is necessary in order to form an iron sulphide-passivating layer on steel which prevents iron oxidation and makes possible pyrrole polymerisation [16]. However, using 0.1 M tosylic acid (Table 2) there was low pigment incorporation. The galvanostatic current efficiency in the presence of zinc phosphate was also low (40%). As noticed for TiO_2 incorporation into PPy matrix [8, 9], polymerisation time is an important factor for greater pigment incorporation. This is one of the reasons for the very low pigment incorporation at short polymerisation times, besides the unfavourable chemical interaction of zinc phosphate with tosylic ions.

Current densities of 5 and 10 mA cm^{-2} and 10 and 20 min of polymerisation were used for experiments in 1 M sodium salicylate. Tables 3 and 4 show that this was the only medium where it was possible to achieve a considerable concentration of zinc phosphate pigment in the PPy matrix.

According to Table 3, high concentration of sodium salicylate (1 M) favours pigment incorporation and increasing polymerisation time from 10 to 20 min does not significantly increase pigment concentration in PPy matrix. However, the increase in pigment concentration

Table 2. Zinc phosphate pigment weight percentage in PPy matrix (C_c)

Polymerisation time/min	C_e/g l^{-1}	C_c/Zn weight %	C_c/PO_4 weight %
3	20	0.2	0.4
4	30	0.05	0.3
4	40	0.2	0.1

Electrolyte: 1 M tosylic acid and 0.5 M pyrrole. C_e – pigment concentration in the electrolyte; $j = 50$ mA cm^{-2}.

Table 3. Zinc phosphate pigment weight percentage in PPy matrix (C_c)

Sodium salicylate concentration/M	Polymerisation time/min	C_e/g l^{-1}	C_c/Zn weight %	C_c/PO_4 weight %
0.1	10	5	1	0
0.1	20	5	1.2	0.3
0.1	20	10	1.2	0.3
1	10	10	2.3	0.4
1	10	20	4.6	1.1
1	20	10	2.5	0.3
1	20	20	3.5	0.9
1	20	20	4	1.1

Electrolyte: sodium salicylate and 0.5 M pyrrole. C_e – pigment concentration in the electrolyte, $j = 10$ mA cm^{-2}.

Table 1. Zinc phosphate pigment weight percentage in PPy matrix (C_c)

Electrolyte	j/mA cm^{-2}	C_e/g l^{-1}	C_c/Zn weight %	C_c/PO_4 weight %
0.1 M KNO_3, 0.1 M pyrrole	5	20	0.1	1.5
0.1 M KNO_3, 0.1 M pyrrole	10	10	0.018	1.2
0.1 M KNO_3, 0.5 M pyrrole	10	20	0.05	0.7
0.1 M KNO_3, 0.5 M pyrrole	10	10	0.04	0.8
0.1 M $H_2C_2O_4$, 0.5 M pyrrole (pH 6.0)	5	20	0.5	0.5

Polymerisation time: 20 min for KNO_3 and 30 min for $H_2C_2O_4$ (pH 2) electrolyte. C_e – pigment concentration in the electrolyte.

Table 4. Zinc phosphate concentration in PPy matrix (C_c) as a function of its concentration in the electrolyte (C_e)

C_e/g l^{-1}	C_c/Total Zn weight %	C_c/Solid Zn weight %	C_c/Soluble Zn weight %	C_c/PO_4 weight %	Total Zn/PO_4 Ratio
10	2.3	0.6	1.7	0.4	5.7
20	4.5	1.7	2.8	1.2	3.7
40	10	6	4	4.3	2.3
80	8	5.3	2.7	3.8	2.1

in the electrolyte (up to approximately 40 g l^{-1}) yields an increase in the pigment content in PPy matrix (Table 4). Above this concentration there is saturation in the degree of incorporation. Using the experimental conditions of 10 mA cm^{-2} and 10 min, high current efficiencies were obtained, around 98%. PPy/zinc phosphate composite films with a thickness of around 27 μm and showing an excellent adhesion to the metallic substrate (Grade Gr0 as DIN 53151) were produced.

Zinc phosphate pigment incorporation is not a simple process of solid incorporation. The experimentally obtained Zn/PO_4 mass ratios, Table 4, were greater than that corresponding to the solid pigment (Zn/PO_4 ratio = 1.4 [12]). This could indicate that the pigment can be incorporated from a soluble fraction (ionic form) since zinc phosphate is partially soluble in sodium salicylate, besides its incorporation into the solid form. The zinc ions can form a complex with salicylate ion and be inserted in PPy matrix as counter-ions. The incorporation of transition metal complexes as counter-ions in PPy matrix is described in the literature [17]. This incorporation depends only on complex stability in the electrolytic medium.

With the quantitative analyses of PO_4 and total Zn ions present in each case of Table 4, the Zn concentration in solid form using pigment stoichiometry [12] was estimated. It was assumed that all phosphate ions were incorporated in solid form. The zinc excess is in ionic (soluble) form. Thus, for a concentration of 40 g l^{-1} of zinc phosphate in the electrolyte, PPy/zinc phosphate composites containing 4% of phosphate and 10% of zinc (total zinc) were obtained. The total zinc concentration is distributed in 6% of zinc in solid form and 4% (zinc excess) of soluble zinc. The Zn/PO_4 mass ratio in the PPy composite approaches zinc phosphate pigment stoichiometry as the pigment concentration in the electrolyte increases. Thus, the Zn solid incorporation is greatly facilitated by the increase in pigment concentration in the electrolyte and the incorporation of Zn ions remains relatively constant throughout the film until saturation in the PPy matrix.

3.2. *XPS and SEM analysis*

XPS and SEM analysis were performed with PPy/zinc phosphate composite films synthesised in an electrolyte containing 1 M sodium salicylate and 0.5 M pyrrole and applying 10 mA cm^{-2} for 10 min. The XPS zinc spectrum (Figure 5) displays doublets or triplets at 1020.5–1023.2 eV ($Zn2p^{3/2}$) and at 1045 eV ($Zn2p^{1/2}$). These doublets or triplets disappeared after 2 h of Ar^+ ion bombardment. The presence of these signals also indicates that zinc is dispersed in the PPy matrix in two forms. One is conductive since it is not subject to any surface charging and is directly bonded to PPy matrix as counter-ion. The other is non-conductive, as shown by the shift in binding energy due to surface charging. The latter is situated between the polymer concavities and is formed by mechanically fixed solid particles.

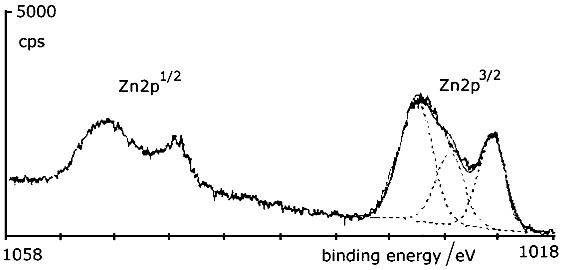

Fig. 5. Zn 2p XPS spectrum of PPy/zinc phosphate composite film before ion bombardment.

In order to analyse zinc phosphate distribution inside the PPy matrix, samples of the composite film were submitted to Ar^+ ion bombardment. After 2 h of ion bombardment, the signal corresponding to the non-conductive form disappeared. So, the non-conductive form is only found at the upper layers in a heterogeneous distribution whereas the conductive form appears throughout the composite films in a reasonably homogeneous distribution, but with a smaller concentration than the non-conductive form, as shown by Figure 6.

SEM images revealed zinc phosphate distribution at the PPy surface (Figure 7). The white dots represent zinc phosphate pigment. It is observed that this pigment is incorporated in agglomerated form and is less homogeneously distributed than TiO_2 in PPy matrix [9, 18].

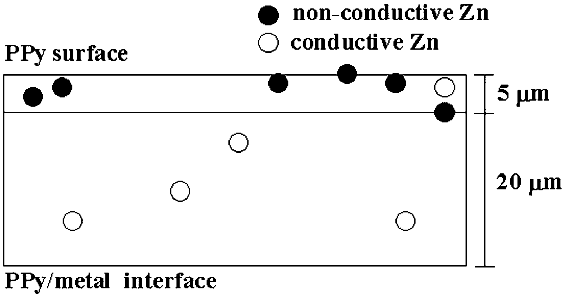

Fig. 6. Schematic representation of zinc phosphate distribution in PPy matrix.

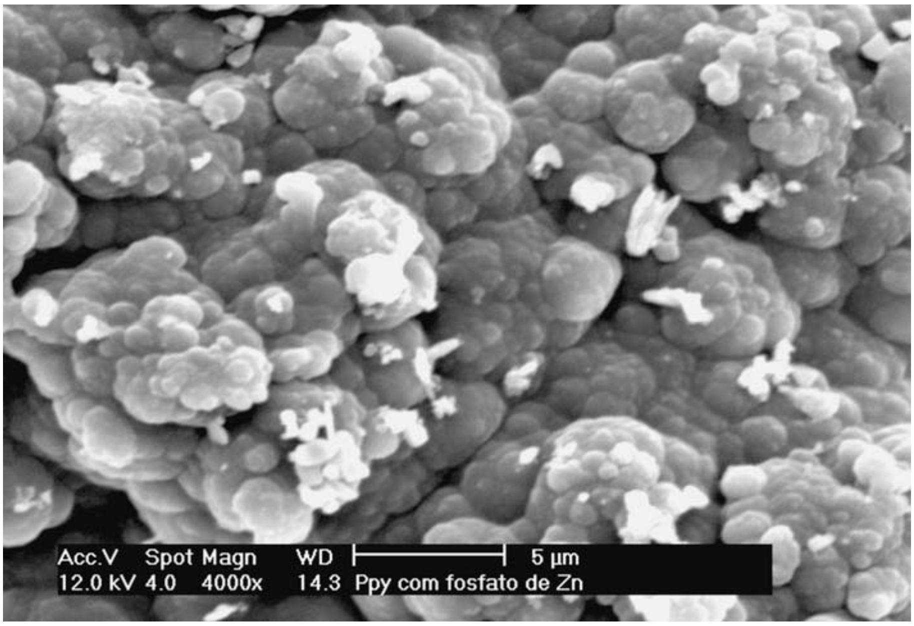

Fig. 7. SEM image of the PPy/zinc phosphate composite film.

3.3. *Zinc phosphate pigment grinding*

The difficulty in reducing the average size of zinc phosphate particles has already been reported [19]. After 5 h of grinding, the average diameter was reduced to 0.55 μm. The particle morphology changed from lamellar to spherical as observed by SEM. Also, the incorporation of grounded pigment was lower than that of the non-ground pigment into PPy matrix and the Zn/PO_4 ratio was greater. These observations indicate that surface modifications were generated during the grinding process such as surface electric charges changing and/or water and CO_2 absorption. Thus, the pigment surface characteristics also have a great influence in the pigment incorporation.

4. Conclusions

Zinc phosphate pigment is not an inert pigment like TiO_2. As observed, it was not possible to form continuous PPy layers on mild steel in oxalic acid medium in the presence of the pigment. Zinc phosphate pigment is partially soluble and the ions present in this medium can hinder PPy formation. In other electrolytic media like KNO_3 and tosylic acid, there was not a considerable incorporation of zinc phosphate under optimum polymerisation conditions. Sodium salicylate was the only medium in which PPy/zinc phosphate composite film was synthesised with high polymerisation current efficiency and showed an appreciable amount of zinc phosphate pigment in polymeric matrix.

Zn and PO_4 quantitative analysis and XPS analysis showed that zinc phosphate is incorporated in two ways into PPy matrix: in solid form, mainly at the external layers of the polymer in a heterogeneous distribution, and as counter-ion, incorporated from soluble Zn species in the electrolyte medium and homogeneously distributed inside the film but in small quantity.

Thus, many chemical and electrochemical factors are involved in the incorporation and distribution of this pigment into PPy matrix such as pigment solubility, complexes formation between electrolyte metal ions and pigment, and competition between corrosion of steel and pyrrole polymerisation.

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