Distribution analysis of TiO$_2$ and commercial zinc phosphate in polypyrrole matrix by XPS

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Abstract

TiO$_2$ as well as a commercial zinc phosphate pigment were incorporated to the PPy matrix during its electropolymerisation on mild steel. Their distribution in the composite films (PPy/TiO$_2$ and PPy/zinc phosphate) was examined by X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). Chemical and electrochemical factors had different influences on their distribution within the PPy matrix. XPS analysis showed that TiO$_2$ is found throughout the PPy films and it is uniformly distributed onto the surface, conversely to zinc phosphate. The latter is present in two heterogeneously distributed forms; (1) a conductive soluble minority and (2) a non-conductive non-soluble majority. The minority form is probably inserted from the soluble species in a complexed form and plays a counter-ion role.

Keywords: Polypyrrole; Titanium dioxide; Zinc phosphate; Composite films; XPS

1. Introduction

A variety of oxides such as WO$_3$, SiO$_2$, TiO$_2$ have been incorporated to the PPy in order to change or improve its properties. Yoneyama et al. [1,2] were the first to attempt a codeposition of TiO$_2$ and WO$_3$ in the PPy matrix using the inert electrodes made of Au or ITO in an electrolytic system without stirring and using a suspension with a pH value higher than the isoelectric point of the oxides. In these conditions, it was obtained an incorporation of 1.15% TiO$_2$ by weight in the PPy matrix.

More recently, Beck et al. [3] showed that the strong convection is an important factor for TiO$_2$ incorporation in the PPy. This solved the problem of TiO$_2$ sedimentation and a TiO$_2$ concentration up to 17% by weight in the composite have been reported when platinum or stainless steel were used as the working electrodes in LiClO$_4$ aqueous medium.

The authors previous work [4] has shown that TiO$_2$ incorporation into the PPy matrix during its electrochemical synthesis on AISI 1010 steel leads to the formation of PPy/TiO$_2$ composite, containing up to 6.5% TiO$_2$ by weight using magnetic electrolyte stirring.

The aim of this work is to understand the mechanism of incorporation of TiO$_2$ and commercial zinc phosphate into the PPy matrix and the analysis of their distribution within the films. These composite films were obtained by the electrochemical synthesis on mild steel under the strong electrolyte stirring. The relationship between pigment distribution and anticorrosion properties of the PPy films, as well as details of polymerisation procedures and pigment concentration analyses [5], will be reported in future publications.

2. Experimental

2.1. Electrochemical synthesis of the PPy/pigment composite films

Sheets of AISI 1010 steel measuring 100 mm × 20 mm × 1 mm were used as the working electrodes. The pyrrole monomer (Aldrich) was bidistilled. The electrolytes used were 0.1 M oxalic acid for the synthesis of the PPy/TiO$_2$ composite film and 1 M sodium salycilate for the PPy/zinc phosphate composite film. The average particle size of titanium dioxide (Merck) was 0.76 and 2.5 μm for commercial zinc phosphate (Hans Heubach).

A looping electrolyte stirring system of the electrolyte, similar to the one described by Beck et al. [3], was employed. All the synthesis were galvanostatically performed and the polymerisation conditions used were
30 min and 5 mA/cm² for obtaining PPy/TiO₂ composite film and 10 min and 10 mA/cm² for PPy/zinc phosphate composite film. Composite films were produced with the thickness in the range of 25–28 μm. After the synthesis, some polymeric samples were dissolved with concentrated sulphuric acid and the elements titanium, zinc and phosphorus were quantitatively analysed by the appropriate spectroscopic techniques.

2.2. X-ray photoelectron spectroscopy and scanning electron microscopy

A SSI X100 photoelectron spectrometer with an aluminium monochromatic source (Al Kz radiation 1486.6 eV), a vacuum of 10⁻⁹ Torr, a spot size of 600 nm and an analytical angle of about 90° with respect to the sample surface was used. Ar⁺ ion bombardment was applied for removing thin layers of the composite films using an AG2 ion gun from Vacuum Generators. The conditions of bombardment were: 4.8 kV of acceleration voltage, a pressure of 5 × 10⁻⁶ mbar and 200 μA of ion beam current. The sputtering rate was approximately 2.5 μm per hour as estimated from the calculated and measured thickness of the composite films. SEM was performed with a PHILIPS XL20 scanning electronic microscope.

The composite film thickness was measured using a FISCHER model DUALSCOPE® MP 20 coating thickness meter.

3. Results and discussion

In the optimum polymerisation conditions, it was obtained samples containing around 14% by weight of TiO₂ or zinc phosphate. Each steel sample was cut into three parts and numbered from the bottom (part 1) to the top (part 3). The pigment distribution was then studied using three parts and numbered from the bottom (part 1) to the top (part 3). The pigment distribution was then studied using XPS.

3.2. TiO₂ distribution in PPy/TiO₂ composite film

For the PPy/TiO₂ composite films, a signal of titanium at the surface of the PPy/TiO₂ composite film was observed before the Ar⁺ ion bombardment (459 eV for Ti₂p 3/2 and 465 eV for Ti₂p 1/2).

The Ti/C intensity ratio at the surface of the PPy/TiO₂ composite films is shown in Table 1. It can be observed that the three parts of each sample (2 cm × 2 cm each) showed a constant Ti/C ratio. Thus, as Ti is uniformly distributed, any part of the sample is representative of the entire sample.

After 2 h of Ar⁺ ion bombardment—equivalent to 5 μm composite film removal—the amount of titanium as TiO₂ slightly increased. Further exposure to Ar⁺ ion bombardment led to a decrease of the TiO₂ concentration within the film. Fig. 1 shows a representation of the TiO₂ distribution in the PPy/TiO₂ composite film.

SEM micrographs showed the presence of TiO₂ homogeneously distributed onto the surface of the PPy/TiO₂ composite film.

3.2. Zinc phosphate distribution in the PPy/zinc phosphate composite film

The Zn 2p doublet was observed in the XPS spectra of the PPy/zinc phosphate composite films at 1020.5–1023.2 eV (Zn 2p 3/2) and 1045 eV (Zn 2p 1/2). In both the regions, other signals were observed. These doublets or triplets disappeared after 2 h of Ar⁺ ion bombardment. These signals indicate that the zinc is dispersed in the polymer in two distinct forms: one is conductive, as indicated by the fact that its binding energy is not affected by the charging effects. This signal is at 1020.5–1023.2 eV and is attributed to the zinc fixed as counter-ion of PPy through several mechanisms. The other Zn signals are assigned to a non-conductive form, as shown by the shift in binding energy due to the charging. They are observed only at the superficial layers of the composite film, representing solid particles of zinc phosphate mechanically fixed to the polymer.

The incorporation of conductive form of Zn might correspond to a small quantity of soluble zinc present in the electrolyte that could be complexed with sodium salicylate and incorporated into the PPy matrix during polymerisation. This form of zinc is present throughout the film. The incorporation of transition metal complexes as counter-ion into the PPy matrix was already described in the literature [6]. The number of anionic complexes of transition metals that can be electrochemically incorporated into the PPy depends primarily on the electrochemical stability of these species.

Table 1

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<thead>
<tr>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
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<tr>
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<td>3</td>
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Fig. 1. Schematic representation of TiO₂ particles distribution in the PPy matrix for the PPy/TiO₂ composite film.

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The distribution of the zinc phosphate at the polymeric surface is presented in Table 2, which shows the Zn/C intensity ratio. This experiment was carried out with the samples containing approximately 14% by weight of zinc phosphate.

The analysis of the results presented in Table 2 has shown that there is no uniform distribution of zinc phosphate at the polymer surface. A considerable difference was observed in the Zn/C ratio for parts 1, 2 and 3 of both the samples. In addition, SEM image showed a more heterogeneous distribution of the pigment onto the surface of PPy than TiO₂ distribution in the PPy matrix. Also, the zinc phosphate particles are almost totally incorporated into the agglomerated form.

The analysis of the results obtained by the ion sputtering of these samples has shown that after approximately 2 h of Ar⁺ ion bombardment, when a fast decrease in the zinc content takes place, a steady amount of zinc in the composite film remains. After this time, non-conductive zinc signal disappears in the XPS spectra. Thus, only conductive zinc is present in the internal layers of the composite film. Fig. 2 shows a representation of zinc phosphate distribution in the PPy matrix.

Quantitative analysis of the composite films has shown that Zn/PO₄ ratio in the composite film was higher than that supplied by the manufacturer of the pigment [7], which is about 1.4. For instance, for the composite films containing 14% of zinc phosphate, a 2.3 ratio was observed, showing that there is more Zn than PO₄ in the polymer matrix. It was confirmed that, in these samples, 10% are due to the mechanical incorporation of the solid pigment and 4% are due to the incorporation of the soluble Zn species.

<table>
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<tr>
<td>Zn/C</td>
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Fig. 2. Schematic representation of zinc phosphate particles distribution in the PPy matrix for the PPy/zinc phosphate composite film.

Pyrrrole electropolymerisation carried out in the presence of zinc phosphate during 20 min produced composite films twice as thick as composite films, synthesised with 10 min polymerisation time. Nevertheless, both films showed the same zinc phosphate weight percentage, differently from the case of TiO₂ incorporation into the PPy, where increasing the polymerisation time by twice led to more than two-fold increase in the pigment concentration.

Beck and Dahlhaus [8] demonstrated that the smaller particle size favours the codeposition process. It is to be expected that the smaller particles are easily codeposited and that larger particles are not permanently incorporated.

The difficulty in reducing the average diameter of zinc phosphate particles has already been reported [9]. After 5 h of grinding in an agate mortar with an automatic pestle, the average diameter was reduced to 0.55 µm. The particle morphology, observed by SEM, changed from the lamellar to the spherical form and the pigment colour changed from white to slightly yellow. During pyrrrole polymerisation there was an agglomeration of the ground pigment. These observations indicated that there was an active surface change during grinding. However, it is probable that this phenomena was due to a surface modification during grinding, such as the change in the surface electric charges and/or water and CO₂ absorption changing the incorporation mechanism of the zinc phosphate to the PPy. This explains that Zn/PO₄ ratio was greater in those composite films than it was in composite films synthesised with non-ground pigment and their lower incorporation degree that was around 6% by weight. Thus, these samples were not analysed by XPS.

4. Conclusions

The distribution of those two pigments in the PPy matrix is quite different. There are many chemical, physical and electrochemical factors involved such as pigment solubility, particle size and complex formation between electrolyte and zinc phosphate. Zinc phosphate is not completely inert as TiO₂ in the electrolytic medium. Although composite films were formed in the presence of TiO₂ in oxalic acid medium, there is no PPy formation using zinc phosphate. Also, some soluble zinc species act as the counter-ion in pyrrrole polymerisation in sodium salicylate medium, indicating that these two pigments are incorporated through different mechanisms.

For PPy/TiO₂ composite films, XPS and SEM images showed that TiO₂ pigment is located mainly at the upper layers of the PPy matrix. Its homogeneous distribution at the polymer surface possibly decreases the number of porous of the polymer.

By quantitative analysis of Zn and PO₄ and by XPS and SEM analysis, it was concluded that zinc phosphate is incorporated in the PPy matrix in two ways: in a solid
heterogeneously distributed form found at the outer layers of the polymer and as counter-ion from the soluble Zn species in the electrolyte. This soluble form is distributed throughout the film but is present in smaller quantity than in the solid form. Work is in progress to increase the homogeneity of zinc phosphate distribution in the PPy matrix in order to improve the composite performance under duress to a rigorous anticorrosion performance test.

Acknowledgements

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References